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VALIDATION OF EMISSION TEST METHOD FOR PCDDs AND PCDFs II

by

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16. ABSTRACT

A modified EPA Method 5 (MM5) sampling train and a dynamic spiking system were used to characterize the precision and accuracy of the collection and analysis of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzo-furans (PCDFs) in municipal waste combustor (MWC) emissions. Isotopically labeled PCDD and PCDF compounds were dynamically spiked into the sampling train during the MWC flue gas sampling in addition to the spikes directly into the XAD-2 resin component of the MM5 sampling train just prior to sampling.

The results from this study indicate that the sampling trains provide quantitative and reproducible measurements of PCDDs and PCDFs under the conditions used during this study. Accuracy of the measurements, estimated from the dynamic spiking system, ranged from 77.6% to 117%. The pooled relative standard deviations of the difference in recovery were between 5.77% to 12.3% for different compounds.

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, North Carolina, has responsibility for assessment of environmental monitoring technology and systems for air, implementation of Agency-wide quality assurance programs for air pollution measurement systems, and supplying technical support to other groups in the Agency including Office of Air and Radiation, the Office of Toxic Substances, and the Office of Solid Waste.

PCDDs and PCDFs are being evaluated for future emissions regulations because of their high toxicities. Acceptable measurement methodology is critical for proper assessment of the impact on the environment of these emissions from stationary sources. Development and validation of measurement methods are key components for producing an acceptable method. This study was undertaken to perform development and validation work on a method for the quantification of PCDD and PCDF emissions from stationary sources.

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PREFACE

This report was prepared for the Environmental Monitoring Systems Laboratory under EPA Contract No. 68-02-4395, Work Assignment No. 23. The objectives of the study were to assess the precision and accuracy of a modified EPA Method 5 sampling system for determining polychlorinated dibenzo-*p*-dioxins and dibenzofurans in municipal waste combustor emissions. The MRI Work Assignment Manager is Dr. John T. Coates. Dr. George Scheil is the Field Crew Chief. Dr. Andrés A. Romeu is the Task Leader for the analytical work and is also the author of this report.

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February 1, 1990

CONTENTS

	Page
Foreword	iii
Preface	iv
Figures	vi
Tables	vi
1. Introduction	1
2. Conclusions and Recommendations	4
3. Methods	5
3.1 Field testing	5
3.2 Analysis methods	7
4. Results and Discussion	12
4.1 Observations from field activities	12
4.2 Static spike recovery	12
4.3 Dynamic spike recovery	14
4.4 Statistical analysis	37
5. Quality Assurance/Quality Control	45
5.1 Surrogate recoveries	45
5.2 Blank trains	45
5.3 Spiked blanks	45
5.4 Quality control check sample	45
5.5 Instrument calibration	49

FIGURES

Number		Page
1	MM5 sampling train configuration used during the study.....	6
2	Dynamic spiking system configuration relative to the MM5 sampling train.....	8
3	Distribution of (a) dynamic spikes and (b) native PCDD/PCDFs in MM5 sampling trains recovered during runs 28 to 33.....	36
4	Distribution of (a) dynamic spikes and (b) native PCDD/PCDFs in MM5 sampling trains recovered during runs 18 to 21.....	38

TABLES

Number		Page
1	Runs 28 to 33 test matrix.....	9
2	Specific dioxins and furans analyzed for runs 28 to 33.....	10
3	Recoveries of static spike during runs 28 to 33.....	13
4	Recoveries of compounds dynamically spiked at 25 ng at the inlet sampling location during runs 28 to 31.....	15
5	Recoveries of compounds dynamically spiked at 100 ng at the inlet sampling location during runs 30 to 33.....	17
6	Recoveries of compounds dynamically spiked at 25 ng at the outlet sampling location during runs 28 to 31.....	19
7	Recoveries of compounds dynamically spiked at 100 ng at the outlet sampling location during runs 30 to 33.....	22
8	Mass of native PCDD/F recovered--run 28.....	24
9	Mass of native PCDD/F recovered--run 29.....	26
10	Mass of native PCDD/F recovered--run 30.....	28

CONTENTS (continued)

		Page
11	Mass of native PCDD/F recovered--run 31.....	30
12	Mass of native PCDD/F recovered--run 32.....	32
13	Mass of native PCDD/F recovered--run 33.....	34
14	Analysis of variance results using dynamic spike recovery as the dependent variable.....	40
15	Net effects of sources of variation on dynamic spike recoveries using analysis of variance model.....	41
16	Analysis of variance results using the difference between 100% and dynamic spike recovery as the dependent variable.....	43
17	Net effects of sources of variation on the difference between 100% and dynamic spike recoveries using analysis of variance model.....	44
18	Method internal standard (surrogate) recoveries.....	46
19	MM5 field blank trains.....	47
20	Spiked blank recoveries.....	48
21	Quality control check sample recoveries.....	48
22	Initial and continuing calibration data for ^{13}C-labeled PCDD/PCDFs (first curve, 3/30/89).....	50
23	Initial and continuing calibration data for ^{13}C-labeled PCDD/PCDFs (second curve, 4/27/89).....	51
24	Initial and continuing calibration data for ^{13}C-labeled PCDD/PCDFs (third curve, 5/8/89).....	51
25	Initial and continuing calibration data for native PCDD/PCDFs.....	52

SECTION 1

INTRODUCTION

A modified EPA Method 5 (MM5) sampling train, incorporating an ice water-chilled condenser and XAD-2 resin cartridge, has been used to collect medium volatility organic compounds from stack gases for a wide variety of combustion sources. The configuration and operating procedures for this system in determining polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in municipal waste combustor (MWC) emissions were standardized by a workshop sponsored by the American Society of Mechanical Engineers (ASME), the U.S. Environmental Protection Agency, and the U.S. Department of Energy held in September 1984. The product of the workshop was a draft sampling and analysis procedures document known as the ASME protocol.

The ASME protocol has become a *de facto* industry standard for sampling stack gases for PCDDs, PCDFs, PCBs, and many other semivolatile organics. Preliminary pilot and field evaluation studies indicated low recoveries of specific PCDD isomers spiked into MM5 sampling trains. In order to supplement the results of those studies, additional experiments were conducted to determine the precision and accuracy of the MM5 system for collecting and recovering PCDD and PCDF emissions.

The overall objective of this study was to characterize the precision and accuracy of the MM5 sampling system using stable, isotopically labeled PCDD and PCDF compounds which were statically and dynamically spiked into the sampling train during MWC flue gas sampling. The following definitions are pertinent to the results reported herewith:

- Static spike--^{13}C-labeled congener spiked directly into the XAD-2 resin component of the MM5 sampling train just prior to sampling. For this study, the compound spiked was ^{13}C-1,2,3,7,8-PeCDF. The purpose of the static spike is to monitor the sampling accuracy of the XAD-2 resin component of the MM5 sampling train.

- Dynamic spike--^{13}C-labeled congeners spiked directly into the flue gas stream being sampled by the MM5 sampling train. The compounds spiked are representative of the full range of native PCDD/PCDFs and include ^{13}C-1,2,3,4-TCDD, ^{13}C-1,2,3,7,8,9-HxCDD, ^{13}C-OCDD, ^{13}C-1,2,3,4,7,8-HxCDF, and ^{13}C-OCDF. The purpose of the dynamic spike is to monitor the sampling accuracy of the MM5 sampling train.

- Native compounds--Non-^{13}C-labeled PCDD/PCDFs.

- Labeled compounds--^{13}C-labeled PCDD/PCDFs used for spiking (static and dynamic) of the MM5 sampling train, as well as those spiked into the sample prior to solvent extraction (surrogates) and analysis (internal standards).

This study was conducted in several iterative phases which were reported to the Office of Air Quality Planning and Standards on June 20, 1989.[1] The previously reported phases can be summarized as follows:

- Phase 1 (runs 1 to 3)--Design and testing of a dynamic spiking system for continuously introducing ^{13}C-labeled PCDD/PCDF congeners into the MM5 train during sampling. Sampling of ambient air using the dynamic spiking system indicated that the development of the system was successful and that it could be used as a field spiking technique.

- Phase 2 (runs 4 to 11)--Laboratory (using ambient air) and field tests (using MWC flue gas) to determine method reproducibility and accuracy of PCDD/PCDF sampling and analysis using the MM5 sampling train and the dynamic spiking system. The laboratory tests indicated adequate recovery of the spiked compounds, but the field test results gave low recoveries of the dynamically spiked components.

- Phase 3--Laboratory studies were conducted to investigate the influence of extraction solvents and unburned carbon content from MWC ash. The results of this phase indicated that toluene is a more efficient extraction solvent for PCDD/PCDFs than dichloromethane, which had been used during Phase 2 of the study.

- Phase 4 (runs 12 to 17)--Laboratory tests were performed to investigate sample recovery enhancement techniques for PCDD/PCDFs from the MM5 sampling train. Toluene was used as the extraction solvent instead of methylene chloride. Additionally, the back-half glassware of the MM5 sampling train was coated with Apiezon-L grease in an attempt to enhance PCDD/PCDF recovery from the back-half components of the train. The results indicated that both sample recovery enhancement techniques employed were successful.

- Phase 5 (runs 18 to 21)--Field tests were conducted using the enhancement techniques elucidated during Phase 4 with an MWC flue gas background. In addition, the distribution of PCDD/PCDFs within the sampling train was determined using two different filter box operating temperatures. In general, quantitative recoveries of the dynamically spiked components were obtained using the recovery

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1 Midwest Research Institute (MRI). 1989. "Validation of Emission Test Method for PCDDs and PCDFs," Final Report on Work Assignment No. 23 prepared for Dr. Jimmy C. Pau, Atmospheric Research and Exposure Assessment Laboratory, U.S. EPA, Office of Air Quality Planning and Standards.

enhancement techniques. However, reproducibility was marginal for some of the replicate sampling trains. Increasing the filter box temperature resulted in changes in the distribution of the labeled spiked compounds in the sampling train, but a parallel effect was not noted for the native dioxins and furans.

The specific objectives for the phase of the study hereby reported were to determine the precision and accuracy of the MM5 train sampling system using uncoated MM5 trains with the dynamic spiking system to sample MWC flue gas background. The test runs reported are Nos. 28 to 33.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The results from this phase of the study to determine the precision and accuracy of the MM5 sampling trains using an MWC flue gas background indicates that the sampling trains provide quantitative and reproducible measurements of dioxins and furans under the conditions used during this study. Accuracy of the measurements as determined using the dynamic spiking system developed by MRI ranged from 77.6% to 117%. Precision of the measurements was high as evidenced by low relative percent differences and by the results of statistical tests to measure differences (with one exception) between replicate sampling trains during the measurement of spiked and native dioxins and furans. The distribution of native dioxins and furans within the sampling trains was essentially the same as for the dynamically spiked components.

The dynamic spiking system is a useful tool in the determination of the accuracy of the measurements. It should be considered as a viable alternative to determine method accuracy during trial burns. It does not affect the determination of native dioxins and furans and should not significantly affect analytical costs. Therefore, it is recommended that during trial burns, selected MM5 trains be equipped with the dynamic spiking system in order to assess accuracy of the measurements. This may be included in a revised MM5 sampling and analysis protocol as an additional QA/QC element.

Other related areas that need to be investigated have been suggested by reviewers and other persons. These are:

- Investigate the potential and conditions under which PCDD/PCDF formation could occur in the particulate emission control device between the inlet and outlet sampling ports. This is expected to be a difficult problem in the light that gas phase PCDD/PCDFs tend to sorb to particulates and thus could not be accurately measured.

- Investigate the maximum allowable holding times between sample collection and sample preparation and analysis.

- Evaluate additional field recovery methods.

- Investigate how other parameters (e.g., HCl, particle size distribution, NO_x, etc.) affect PCDD/PCDF sampling and analysis.

SECTION 3

METHODS

The general experimental approach was to measure the recoveries of specific ^{13}C-labeled PCDD and PCDF congeners spiked into MM5 trains during incineration stack gas sampling. Selected ^{13}C-labeled congeners representing tetra- through octachloro PCDD and PCDF homologs were spiked onto the XAD-2 resin prior to each test (static spike) and continuously throughout the test (dynamic spike). Following completion of each test, the samples were recovered from the trains and analyzed for the spiked compounds and for the native PCDDs and PCDFs. Recoveries were determined for each spiked compound by comparing the amount measured against the amount spiked.

3.1 FIELD TESTING

The incinerator selected for this study was a mass-burn waste combustor burning municipal refuse. The same MWC was used during previous phases of the study. Electrostatic precipitators were used to control particulate emissions. Refuse was fed into a reverse reciprocating stoker grate. In addition to the motion of the grates, the underfire grate assisted in further agitation of the waste. The unit was operated without auxiliary fuel.

A total of 6 test runs (including two blank trains sampling ambient air) were conducted during six test days. The sampling trains were not traversed during the test runs but were operated at single, average velocity points. Ports 1 and 2 were the left- and right-hand liners in one dual probe located at the inlet of the electrostatic precipitator. Ports 3 and 4 were in the second dual probe located at the outlet of the precipitator. Sampling was conducted simultaneously at both inlet and both outlet sampling ports. The two trains in each probe had closely matched flow rates, but the total volume of flue gas sampled at the inlet and outlet sampling ports was about 30% apart. All trains (with the exception indicated below) were maintained at isokinetic conditions.

The MM5 sampling system used for this study was essentially the same as described in the draft ASME protocol (Figure 1). The configuration of the condenser and resin cartridges was modified as follows. The water jackets of both components were in the form of impingers. This arrangement made the condenser and cartridge less vulnerable to breakage and facilitated placement of a thermistor at the inlet of the resin. All glassware joints in the train were glass-to-PTFE (Teflon) seals. Other procedural modifications to ASME draft protocol were as follows:

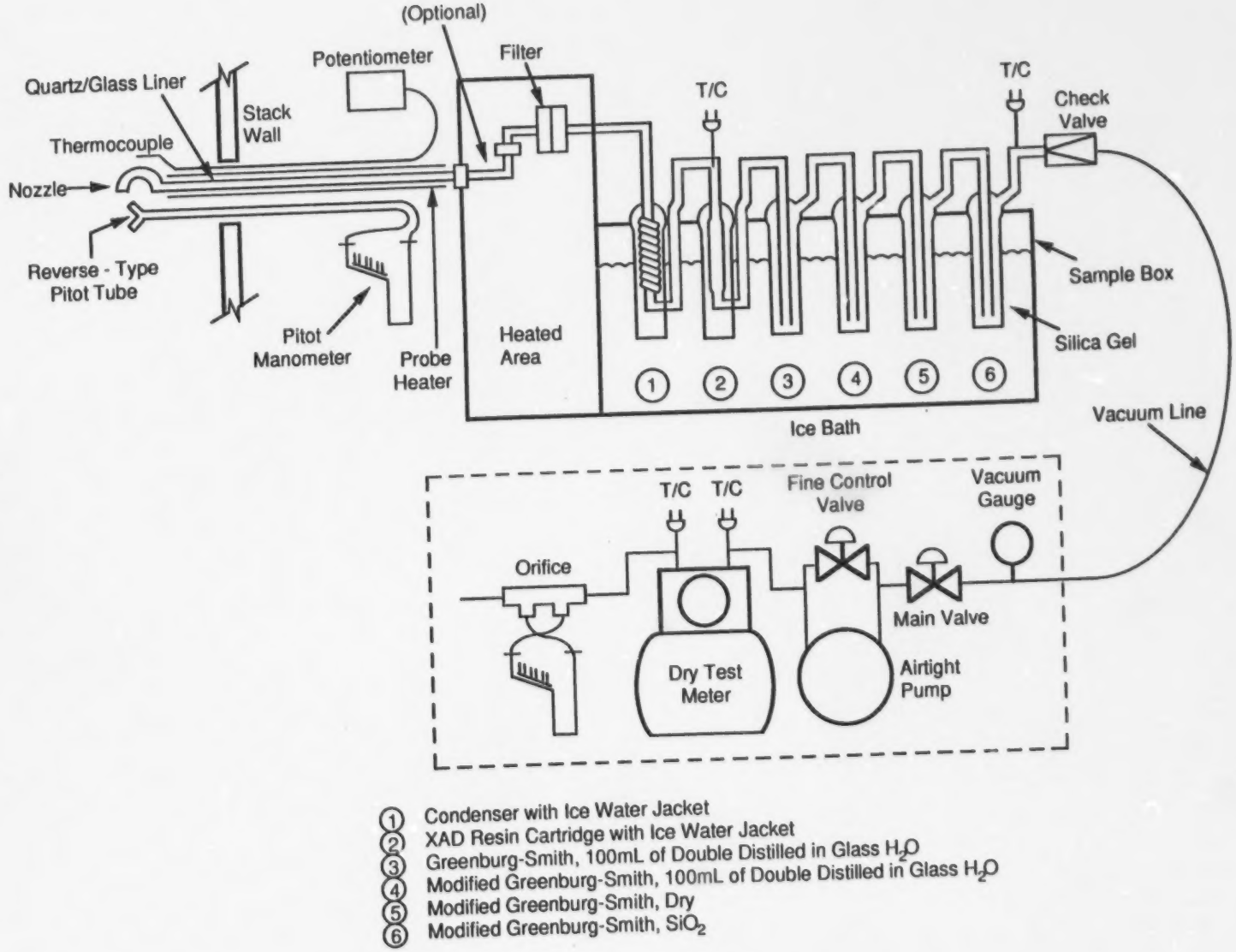

Figure 1. MM5 sampling train configuration used during the study.

- Nickel nozzles were used on the probes.
- Borosilicate glass was used for train components.
- All references to hexane rinses were changed to toluene rinses.
- Toluene was used in place of hexane in the procedure.
- No traversing was performed; samples were collected isokinetically at a single point.
- Blank trains were set up to sample ambient air.
- One blank train was recovered from the inlet location and one from the outlet location.

The field static spiking solution, ^{13}C-1,2,3,7,8-PeCDF, was added to the XAD-2 resin prior to each test. The dynamic spiking solution containing five ^{13}C-labeled PCDD/PCDFs (^{13}C-1,2,3,4,7,8-HxCDF, ^{13}C-OCDF, ^{13}C-1,2,3,4-TCDD, ^{13}C-1,2,3,7,8,9-HxCDD, and ^{13}C-OCDD) was continuously added throughout the test using the dynamic spiking system designed by MRI (Figure 2) described in detail elsewhere.[2] The tests were conducted using two spiking levels: 25 and 100 ng. Each level was spiked in duplicate at each sampling location on two of the test days and once on the other test days. The test matrix is shown in Table 1.

Each sampling train was leak-checked prior to and after collection of the samples. The stack gases were sampled for 240 min. The dynamic spiking system injectors were started 30 min after the start of the test and operated for a total of 180 min. The MM5 trains were disassembled, each section was capped, and the components were taken to a clean area. Each appropriate section of the sampling train was rinsed sequentially with acetone and toluene (3X), the probes brushed, and the rinses stored in amber glass bottles with PTFE-lined screw caps. Particulates (from the cyclone and filter) were stored in bottles and wetted with toluene. The XAD cartridge was sealed.

3.2 ANALYSIS METHODS

Each sample was analyzed for the specific dioxin and furan congeners noted in Table 2. Each component of the MM5 sampling train was individually spiked with a Method Internal Standards mix (i.e., surrogates, namely ^{13}C-2,3,7,8-TCDF, ^{13}C-2,3,7,8-TCDD, ^{13}C-1,2,3,7,8-PeCDD, and ^{13}C-1,2,3,4,6,7,8-HpCDD) prior to solvent extraction. All solvent extractions were conducted using toluene as the extraction solvent. The solid samples (i.e., XAD-2 resin and combined particulates/filter) were Soxhlet-extracted for 16 to 22 h. XAD-2 resin extracts with free water and all front-half and back-half glassware rinses were back-extracted using reagent water (produced using Millipore Milli-Q Reagent Grade Water System). The sample extracts were passed through sodium sulfate to remove residual water.

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[2] Midwest Research Institute (MRI), 1989, op. cit.

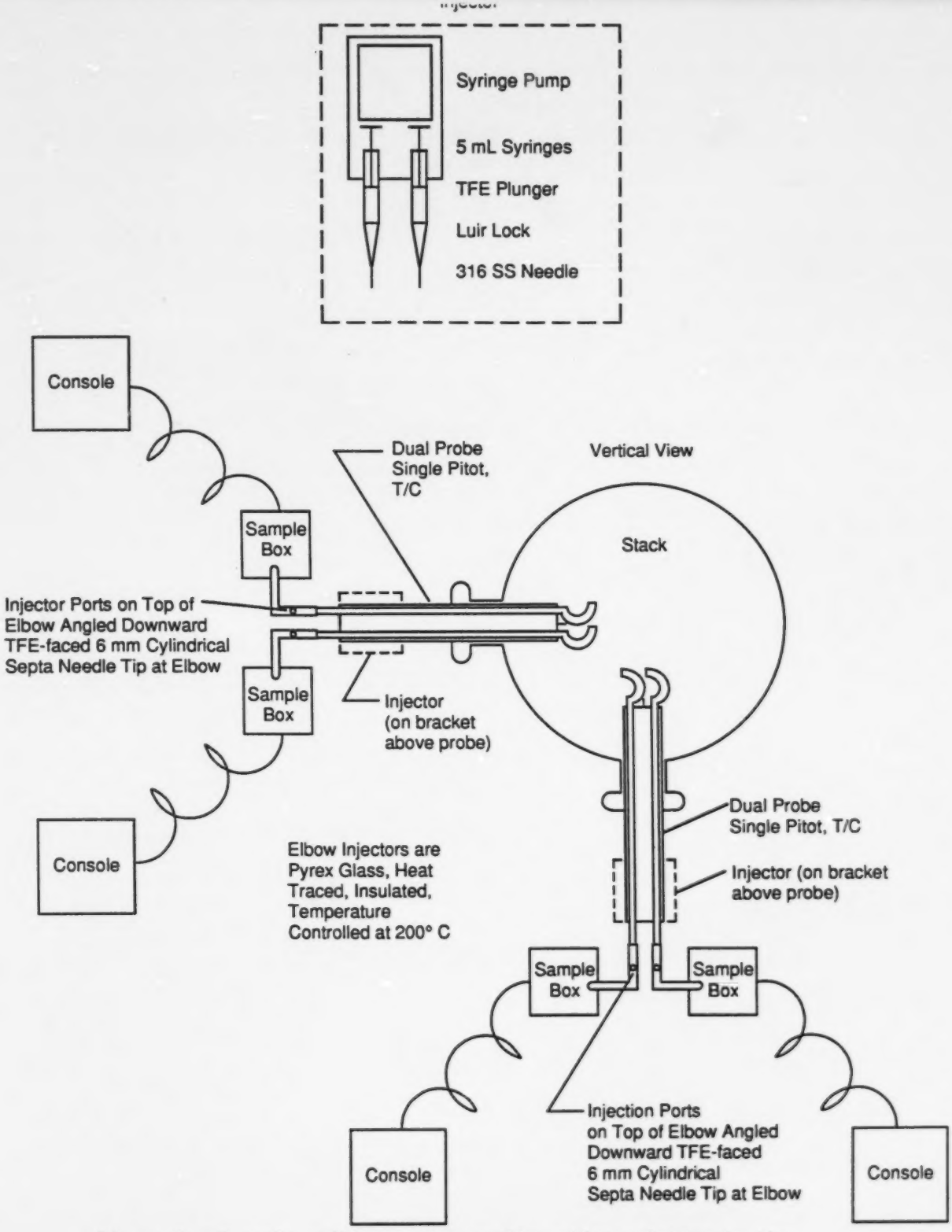

Figure 2. Dynamic spiking system configuration relative to the MM5 sampling train.

TABLE 1. RUNS 28 TO 33 TEST MATRIX

Test day	Run No.	Location: Inlet[a] Port No. 1	Location: Inlet[a] Port No. 2	Location: Outlet[b] Port No. 3	Location: Outlet[b] Port No. 4	Blank
1	28	L[c]	L	L	L	None
2	29	L	L	L	L	Outlet
3	30	L	H[d]	L	H	None
4	31	H	L	H[e]	L[e]	None
5	32	H	H	H	H	Inlet
6	33	H	H	H	H	None

[a] The individual MM5 sampling trains at port No. 1 and port No. 2 of the inlet sampling location represent replicate trains sampling the flue gas simultaneously.

[b] The individual MM5 sampling trains at port No. 3 and port No. 4 of the outlet sampling location represent replicate trains sampling the flue gas simultaneously.

[c] L indicates that the dynamic and static spiking levels for this run were the low levels (i.e., 25 ng).

[d] H indicates that the dynamic and static spiking levels for this run were the high levels (i.e., 100 ng).

[e] These dynamic (but not the static) spiking levels were inadvertently switched by the field crew. Thus, port No. 3 was spiked at the low level, and port No. 4 was spiked at the high level. Laboratory personnel performed surrogate spiking at levels appropriate to the originally planned spiking levels. The effect of this mistake was negligible.

TABLE 2. SPECIFIC DIOXINS AND FURANS ANALYZED FOR RUNS 28 TO 33

Compound	Ion (relative intensity) Primary [M + 2]+	Secondary [M]+	Ratio range
Stable isotopes (field-spiked analytes)			
^{13}C-1,2,3,7,8-PeCDF[a]	351.9005 (100)	349.9035 (61)	0.49-0.73
^{13}C-1,2,3,4,7,8-HxCDF[a]	385.8615 (100)	387.8586 (87)[c]	0.66-0.98
^{13}C-OCDF[a]	455.7806 (100)[c]	453.7836 (87)[d]	0.70-1.04
^{13}C-1,2,3,4-TCDD[a]	333.9344 (100)	331.9373 (76)	0.61-0.91
^{13}C-1,2,3,7,8,9-HxCDD[a]	401.8564 (100)	403.8535 (82)[c]	0.66-0.98
^{13}C-OCDD[a]	471.7755 (100)[c]	469.7785 (87)[d]	0.70-1.04
Native (calibration standard)			
2,3,7,8-TCDF	305.8987 (100)	303.9016 (76)	0.61-0.91
2,3,7,8-TCD	321.8936 (100)	319.8965 (76)	0.71-0.91
1,2,3,7,8-PeCDF	339.8597 (100)	337.8627 (61)	0.49-0.73
1,2,3,7,8-PeCDD	355.8546 (100)	353.8576 (61)	0.49-0.73
2,3,4,6,7,8-HxCDF	373.8207 (100)[b]	375.8178 (82)[c]	0.66-0.98
1,2,3,7,8,9-HxCDD	389.8156 (100)[b]	391.8127 (82)[c]	0.66-0.98
1,2,3,4,6,7,8-HpCDF	407.7817 (100)[b]	409.7787 (98)[c]	0.78-1.18
1,2,3,4,6,7,8-HpCDD	423.7767 (100)[b]	425.7737 (99)[c]	0.79-1.19
OCDF	443.7398 (100)	441.7428 (87)	0.70-1.04
OCDD	459.7347 (100)	457.7377 (87)	0.70-1.04
Stable isotopes (method internal standard)			
^{13}C-2,3,7,8-TCDF	317.9395 (100)	315.9424 (76)	0.61-0.91
^{13}C-2,3,7,8-TCDD	333.9343 (100)	331.9373 (76)	0.61-0.91
^{13}C-1,2,3,7,8-PeCDD	367.8954 (100)	365.8984 (61)	0.47-0.73
^{13}C-1,2,3,4,6,7,8-HpCDD	435.8175 (100)[b]	437.8145 (99)[c]	0.79-1.19
Recovery internal standard			
^{13}C-1,2,3,6,7,8-HxCDD	401.8564 (100)[b]	403.8535 (82)[c]	0.66-0.98

[a] = Quantitation was on the primary ion + secondary ion.

[b] = [M]+.

[c] = [M + 2]+.

[d] = [m + 4]+.

Each extract was rotoevaporated to a final volume of 1 to 2 mL. A small volume (25 µL) of tridecane keeper was added to each extract and then further concentrated using a nitrogen evaporator. Hexane was added to the extracts to a final volume of 1 mL.

A 1 x 10-cm tapered column was slurry-packed in hexane with 1 g of silica gel followed by 4 g of 40% (w/w) sulfuric acid modified silica gel. A second column (1 x 30 cm) was also slurry-packed, but with 6 g of acid alumina followed by 1 g of sodium sulfate, also in hexane. The two columns were set such that the silica gel column drained directly into the acid alumina column. The sample extract was applied to the silica gel column and drawn into the packing together with three rinses of the concentrated extract container. The silica gel column was eluted with 45 mL hexane into the alumina column, which was then eluted with 20 mL hexane. A solution of 20% (v/v) dichloromethane/hexane was used to elute the alumina column (20 mL). Finally, 20 mL of a 50% (v/v) dichloromethane/hexane solution was used to elute the column. The three fractions were collected separately and archived. The 20% dichloromethane/hexane fraction was concentrated to 2 to 3 mL, transferred to a Reacti-vial®, amended with 25 µL of tridecane, and the volume reduced to 25 or 100 µL, depending on the field spiking levels. This cleaned-up extract was spiked with a Recovery Internal Standard solution (^{13}C-1,2,3,6,7,8-HxCDD) and analyzed for PCDD/PCDF by HRGC/HRMS.

A Carlo Erba MFC-500 gas chromatograph was fitted with a 60-m x 0.25-µm i.d. DB5 fused silica capillary column using helium carrier gas (20 to 40 cm/sec). A Grob-type injector in the splitless mode at 270°C was used to inject a 1-µL portion of the sample extract. After 2 min at 200°C, the temperature in the GC was increased to 220°C (5°C/min), held for 16 min, increased again to 235°C (5°C/min) and held for 7 min, and finally increased to 330°C (5°C/min). The capillary column was threaded directly into the source chamber of a Kratos MS-50 high resolution mass spectrometer (transfer line temperature of 280° to 300°C) scanning from 202 to 472 amu in 1 s or less. The resolution on the mass spectrometer was set to 3,000. All samples and standards were analyzed using the selected ion monitoring (SIM) mode. A three-point calibration curve was analyzed and relative response factors calculated. Daily checks of the mass resolution and accuracy, GC retention windows, and calibration were performed. Table 2 presents the ions monitored during data acquisition.

SECTION 4

RESULTS AND DISCUSSION

4.1 OBSERVATIONS FROM FIELD ACTIVITIES

The field crew noted the following observations during the test runs:

- Run 28, sampling port No. 1--The MM5 sampling train failed the posttest leak check. There is no way of knowing at what point the vacuum on the train was broken. The analytical data indicate results consistent with the replicate train, and therefore it is concluded that the leak occurred in the final stages of the run, after a useful sample had been collected.

- Run 30, sampling port No. 2--The MM5 sampling train was 72% isokinetic. The effect of this impacts the particle size distribution sampled. Since particulate loading was not monitored during this study, the impact of this deviation on the results reported is not significant.

- Run 33, sampling port No. 2--A chunk of ash was found on the nozzle. There was no indication that this affected the vacuum system of the sampling train, and thus it is concluded that it did not affect the data presented.

During evaluation of the data, it became apparent that during run No. 31, the field crew inadvertently switched the dynamic spiking levels for sampling port Nos. 3 and 4. Since the static spike was performed in the laboratory prior to the field test, the static spiking levels for these sampling trains were as originally planned.

The samples were collected during June 1988 and the analysis sequence started in February 1989. In the interim period, the samples were stored in a locked, limited access, walk-in cold room (4°C).

4.2 STATIC SPIKE RECOVERY

Results for the recovery of the static spike of a ^{13}C-labeled congener added to the XAD-2 resin prior to sample collection are presented in Table 3. The recoveries of the compound statically spiked onto the XAD-2 resin were somewhat disappointing in light of the recoveries observed during earlier phases of this study.[3] However, given the consistently high recoveries

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[3] MRI. 1989. op. cit.

TABLE 3. RECOVERIES OF STATIC SPIKE DURING RUNS 28 TO 33

Run No.	Spike level (ng)	Sampling location	Sampling port	Percent recovery on XAD resin
28	25	Inlet	1	55.1
			2	34.8
		Outlet	3	57.3
			4	38.8
29	25	Inlet	1	51.4
			2	48.8
		Outlet	3	57.0
			4	63.3
30	25	Inlet	1	52.2
	100		2	78.5
	25	Outlet	3	66.1
	100		4	78.3
31	100	Inlet	1	73.8
	25		2	70.9
	100[a]	Outlet	3	85.8
	25[a]		4	75.8
32	100	Inlet	1	76.7
			2	86.3
		Outlet	3	74.5
			4	67.1
33	100	Inlet	1	75.8
			2	77.3
		Outlet	3	80.3
			4	80.8

[a] The dynamic field spiking levels on these samples were inadvertently switched during the test run, but the static spiking levels used were as originally planned.

observed during those earlier phases, it is believed that the low recoveries observed, especially for runs 28 and 29, were anomalous and, in light of the results presented below, do not represent an accurate view of the sampling accuracy of the MM5 sampling train.

4.3 DYNAMIC SPIKE RECOVERY

4.3.1 Inlet Sampling Port

Table 4 presents the percent recovery of the compounds dynamically spiked at 25 ng into the sampling trains at the inlet sampling ports (runs 28, 29, 30, and 31). The average of all sums of recovery values for the individual congeners spiked into each of the sampling trains analyzed was 95.1% (n = 30, 28% RSD). This average value was obtained from two sets of replicate sampling trains and two sets of individual, nonreplicate sampling trains. The overall average recovery indicates that the sampling train quantitatively collected the dynamically spiked compounds added during the sampling runs.

Runs 28 and 29 were conducted using replicate sampling trains at both inlet ports. Evaluation of the replicate data from a qualitative point of view suggests that for run 28, reproducibility was good, but for run 29, the recoveries from sample location No. 1 were about one-half of that seen for sampling location No. 2. These differences are discussed in greater detail in Section 4.4, Statistical Analysis, of this report. It is suspected that during run 29, the syringe used for dynamic spiking into sampling port No. 1 leaked at the Luer lock fitting, thereby directing an unknown portion of the dynamic spike into the sampling train. This could not be confirmed from field observations, but is a plausible explanation of the results generated. This conclusion is supported by results generated from the analysis of native dioxins and furans, as discussed in Section 4.3.3.

Table 5 presents the results of the recovery of the labeled compounds dynamically spiked into the inlet sampling trains at 100 ng (runs 30, 31, 32, and 33). The average of all sums of recovery values for the individual congeners spiked into each sampling train was 77.6% (n = 30, 24% RSD). This average value was obtained from two sets of replicate sampling trains and two sets of individual, nonreplicate sampling trains. The overall average recovery for the sampling trains dynamically spiked at 100 ng was approximately 20% lower than those spiked at 25 ng.

In summary, recovery of the dynamic spikes for the sampling trains spiked with low (25 ng) levels of labeled congeners was quantitative (95%), whereas the recovery of the dynamic spikes added to the system at 100 ng was somewhat lower (78%), although still quantitative. The reasons for the discrepancy in total recovery between the low-level and high-level dynamic spikes are not immediately apparent.

4.3.2 Outlet Sampling Port

The percent recovery results for compounds dynamically spiked at 25 ng into the MM5 trains in the outlet sampling ports are presented in Table 6 (runs 28, 29, 30, and 31).

TABLE 4. RECOVERIES OF COMPOUNDS DYNAMICALLY SPIKED AT 25 ng AT THE INLET SAMPLING LOCATION DURING RUNS 28 TO 31[a]

Run	Spike level (ng)	^{13}C-labeled analyte	Stack location	Inlet % recovery: Cyclone/ filter	Probe/ front half	Back half	XAD	Sum of recovery
28	25	HxCDF	1	54.8	10.7	3.96	65.4	135
			2	60.0	8.19	1.15	45.0	114
			Average	57.4	9.45	2.56	55.2	125
			RPD[b]	9%	27%	110%	37%	16%[c]
		OCDF	1	84.0	15.7	1.19	8.59	109
			2	91.0	8.37	0.340	7.74	107
			Average	87.5	12.0	0.765	8.17	108
			RPD	8%	61%	111%	10%	2%
		TCDD	1	38.5	7.86	3.76	87.8	138
			2	34.8	6.49	1.94	70.3	114
			Average	36.7	7.18	2.85	79.1	126
			RPD	10%	19%	64%	22%	19%
		HxCDD	1	54.5	10.1	2.25	30.8	97.6
			2	58.1	6.71	1.08	21.7	87.5
			Average	56.3	8.40	1.67	26.2	92.6
			RPD	6%	40%	70%	35%	11%
		OCDD	1	88.8	16.7	1.05	6.62	113
			2	94.1	8.48	0.390	5.80	109
			Average	91.4	12.6	0.720	6.21	111
			RPD	6%	65%	92%	13%	4%
29	25	HxCDF	1	41.8	6.22	0.180	1.38	49.6
			2	77.3	29.6	0.680	3.09	111
			Average	59.5	17.9	0.430	2.24	80.1
			RPD	60%	131%	116%	77%	76%
		OCDF	1	40.0	6.51	0.160	0.460	47.1
			2	66.7	24.1	0.210	0.770	91.8
			Average	53.3	15.3	0.185	0.615	69.5
			RPD	50%	115%	27%	50%	64%
		TCDD	1	43.9	9.20	0.070	1.46	54.6
			2	56.0	28.4	0.450	5.96	90.8
			Average	50.0	18.8	0.260	3.71	72.7
			RPD	24%	102%	146%	121%	50%

(continued)

TABLE 4 (continued)

Run	Spike level (ng)	^{13}C-labeled analyte	Stack location	Inlet % recovery: Cyclone/ filter	Probe/ front half	Back half	XAD	Sum of recovery
29 (continued)	25	HxCDD	1	36.5	4.87	0.720	1.59	43.7
			2	60.0	21.8	0.690	2.43	84.8
			Average	48.2	13.3	0.705	2.01	64.2
			RPD	49%	127%	4%	42%	64%
		OCDD	1	38.2	6.82	0.360	0.190	45.6
			2	70.7	26.9	0.210	0.290	98.0
			Average	54.5	16.8	0.285	0.240	71.8
			RPD	60%	119%	53%	42%	73%
30	25	HxCDF	1	54.2	20.7	2.32	5.80	83.0
		OCDF	1	98.5	9.78	0.250	0.740	109
		TCDD	1	70.0	13.6	3.35	15.0	101.9
		HxCDD	1	57.7	12.4	1.29	3.08	74.4
		OCDD	1	83.9	11.0	0.210	0.170	95.3
31	25	HxCDF	2	70.5	48.2	4.92	13.0	137
		OCDF	2	96.1	24.0	0.610	1.60	122
		TCDD	2	44.4	16.4	5.26	28.9	94.9
		HxCDD	2	64.6	18.8	2.54	6.12	92.0
		OCDD	2	103	22.9	0.480	0.350	126

[a] Only runs 28 and 29 (both trains) and 30 and 31 (single train) were dynamically spiked at the low spiking level.

[b] RPD (relative percent different) = $\frac{\text{Value 1 - Value 2}}{\text{Average of values 1 and 2}}$

[c] The RPD value under the sum of recovery column is relative to the sum of recovery values for each individual train.

TABLE 5. RECOVERIES OF COMPOUNDS DYNAMICALLY SPIKED AT 100 ng AT THE INLET SAMPLING LOCATION DURING RUNS 30 TO 33[a]

Run	Spike level (ng)	^{13}C-labeled analyte	Stack location	Inlet % recovery: Cyclone/ filter	Probe/ front half	Back half	XAD	Sum of recovery
30	100	HxCDF	2	66.9	23.8	2.20	9.03	102
		OCDF	2	55.6	18.4	1.07	5.33	80.4
		TCDD	2	51.5	14.4	2.07	23.9	91.9
		HxCDD	2	56.4	19.4	1.29	6.12	83.2
		OCDD	2	68.1	21.3	0.890	4.87	95.1
31	100	HxCDF	1	76.7	20.9	3.11	13.8	114
		OCDF	1	75.8	21.0	1.38	4.96	103
		TCDD	1	48.1	16.3	3.39	32.0	99.7
		HxCDD	1	72.6	15.5	1.64	7.93	97.7
		OCDD	1	92.4	22.6	0.960	4.26	120
32	100	HxCDF	1	41.2	16.5	0.480	2.03	60.2
			2	71.7	8.48	0.330	1.06	81.6
			Average	56.4	12.5	0.405	1.55	70.9
			RPD[b]	54%	64%	37%	63%	30%[c]
		OCDF	1	35.4	11.1	0.680	3.66	50.9
			2	45.2	8.20	0.370	0.270	54.0
			Average	40.3	9.67	0.525	1.97	52.5
			RPD	24%	30%	59%	173%	6%
		TCDD	1	44.5	12.6	0.980	3.69	61.7
			2	59.6	5.77	0.800	3.05	69.2
			Average	52.0	9.18	0.890	3.37	65.5
			RPD	29%	74%	20%	19%	11%
		HxCDD	1	36.1	11.3	1.62	2.44	51.4
			2	54.8	7.76	1.49	0.840	64.8
			Average	45.4	9.53	1.56	1.64	58.1
			RPD	41%	37%	8%	98%	23%

(continued)

TABLE 5 (continued)

Run	Spike level (ng)	^{13}C-labeled analyte	Stack location	Inlet % recovery: Cyclone/ filter	Probe/ Front half	Back half	XAD	Sum of recovery
32 (continued)		OCDD	1	39.7	12.0	2.41	3.51	57.6
			2	54.1	9.31	0.560	0.270	64.2
			Average	46.9	10.7	1.49	1.89	60.9
			RPD	31%	25%	125%	171%	11%
33	100	HxCDF	1	70.0	9.43	0.520	1.76	81.7
			2	66.0	11.9	0.330	1.43	79.7
			Average	68.0	10.7	0.425	1.60	80.7
			RPD	6%	23%	45%	21%	2%
		OCDF	1	50.5	11.1	0.210	0.150	62.0
			2	48.9	11.7	0.240	0.290	61.1
			Average	49.7	11.4	0.225	0.220	61.6
			RPD	3%	5%	13%	64%	1%
		TCDD	1	74.7	6.55	0.560	4.82	86.7
			2	70.0	9.32	0.250	3.13	82.7
			Average	72.3	7.94	0.405	3.98	84.7
			RPD	7%	35%	77%	43%	5%
	100	HxCDD	1	54.4	8.26	0.550	1.20	64.4
			2	51.3	9.85	0.440	1.59	63.2
			Average	52.9	9.06	0.495	1.40	63.8
			RPD	6%	18%	22%	28%	2%
		OCDD	1	59.4	11.3	0.420	0.370	71.5
			2	58.5	12.8	0.300	0.360	72.0
			Average	59.0	12.1	0.360	0.365	71.8
			RPD	2%	12%	33%	3%	1%

[a] Only runs 30 and 31 (single train) and 32 and 33 (both trains) were dynamically spiked at the high spiking level.

[b] RPD (relative percent different) = $\frac{\text{Value 1 - Value 2}}{\text{Average of values 1 and 2}}$

[c] The RPD value under the sum of recovery column is relative to the sum of recovery values for each individual train.

TABLE 6. RECOVERIES OF COMPOUNDS DYNAMICALLY SPIKED AT 25 ng AT THE OUTLET SAMPLING LOCATION DURING RUNS 28 TO 31[a]

Run	Spike level (ng)	^{13}C-labeled analyte	Stack location	Outlet % recovery				
				Cyclone/ filter	Probe/ front half	Back half	XAD	Sum of recovery
28	25	HxCDF	3	26.9	3.39	6.27	77.8	114
			4	31.6	4.16	3.88	93.9	134
			Average	29.2	3.78	5.08	85.8	124
			RPD[b]	16%	20%	47%	19%	16%[c]
		OCDF	3	48.1	7.44	5.85	41.4	103
			4	44.5	8.91	3.52	43.3	100
			Average	46.3	8.18	4.69	42.3	102
			RPD	8%	18%	50%	5%	2%
		TCDD	3	24.0	3.06	2.94	87.5	117
			4	25.2	3.27	2.21	94.8	125
			Average	24.6	3.17	2.58	91.2	121
			RPD	5%	7%	28%	8%	7%
		HxCDD	3	26.3	3.54	5.38	60.9	96.1
			4	35.3	4.51	3.41	70.3	114
			Average	30.8	4.03	4.40	65.6	105
			RPD	29%	24%	45%	14%	17%
		OCDD	3	54.0	8.31	4.77	40.1	107
			4	52.0	10.7	0.950	40.1	104
			Average	53.0	9.51	2.86	40.1	105
			RPD	4%	25%	134%	0%	3%
29	25	HxCDF	3	80.8	7.70	15.0	33.9	137
			4	92.0	12.3	11.2	27.2	143
			Average	86.4	10.0	13.1	30.6	140
			RPD	13%	46%	29%	22%	4%
		OCDF	3	68.7	14.1	6.11	12.3	101
			4	64.4	18.2	3.91	5.60	92.1
			Average	66.6	16.2	5.01	8.96	96.7
			RPD	6%	25%	44%	75%	9%
		TCDD	3	43.0	7.91	7.58	64.4	123
			4	51.8	13.5	6.42	53.0	125
			Average	47.4	10.7	7.00	58.7	124
			RPD	19%	52%	17%	19%	1%

(continued)

TABLE 6 (continued)

Run	Spike level (ng)	^{13}C-labeled analyte	Stack location	Outlet % recovery: Cyclone/ filter	Probe/ Front half	Back half	XAD	Sum of recovery
29 (continued)	25	HxCDD	3	70.4	7.47	8.18	25.7	112
			4	78.7	11.2	6.14	19.0	115
			Average	74.6	9.34	7.16	22.3	113
			RPD	11%	40%	28%	30%	3%
		OCDD	3	75.3	16.5	5.83	11.7	109
			4	71.8	20.1	4.36	6.56	103
			Average	73.6	18.3	5.10	9.13	106
			RPD	5%	20%	29%	56%	6%
30	25	HxCDF	3	30.4	6.26	25.5	53.2	115
		OCDF	3	64.3	11.0	10.1	18.6	104
		TCDD	3	17.6	6.09	12.4	87.6	124
		HxCDD	3	37.0	6.48	18.0	40.5	102
		OCDD	3	80.1	14.0	8.51	17.8	120
31	25	HxCDF	3	33.4	5.63	18.5	69.4	127
		OCDF	3	94.2	5.94	13.1	39.5	153
		TCDD	3	17.4	3.93	6.64	111	139
		HxCDD	3	41.5	6.05	15.7	55.2	118
		OCDD	3	109	8.22	9.61	38.6	165.4

[a] Only runs 28 and 29 (both trains) and 30 and 31 (single train) were dynamically spiked at the low spiking level.

[b] RPD (relative percent different) = $\frac{\text{Value 1 - Value 2}}{\text{Average of values 1 and 2}}$

[c] The RPD value under the sum of recovery column is relative to the sum of recovery values for each individual train.

The average of all sums of recovery values for the individual congeners spiked into each of the sampling trains analyzed was 112% (n = 30, 12% RSD). This average value was obtained from two sets of replicate sampling trains and two individual, nonreplicate sampling trains. The overall average recovery indicates that the sampling trains quantitatively collected the dynamically spiked compounds added during the sampling runs.

Table 7 shows the recoveries of the labeled compounds dynamically spiked into the outlet sampling trains at 100 ng (runs 30, 31, 32, and 33). The average of all sums of recovery values for these sampling trains was 117% (n = 30, 13% RSD). This average value was obtained from two sets of replicate sampling trains and two individual, nonreplicate sampling trains. The overall average recovery indicates that the sampling trains quantitatively collected the dynamically spiked compounds added during the sampling runs.

In summary, the total recovery was quantitative for the low (25 ng) dynamic spike (112%) and for the high (100 ng) dynamic spike (117%).

4.3.3 Native Dioxins and Furans

The mass of native dioxins and furans recovered is presented in Tables 8 to 13.

The apparent absence of major differences between the amount of native PCDDs/PCDFs recovered from both replicate sampling trains during run 29 (Table 9) supports the conclusion that during this run, the dynamic spike added to the inlet train located at sampling port No. 1 was not added as intended. As was discussed in Section 4.3.1, the dynamic spike recoveries for the inlet sampling trains during this run were different by approximately 100%. It is suspected that the syringe feeding the dynamic spiking solution into one of the replicate trains leaked. This problem can be easily circumvented by using fixed-needle, gas-tight syringes in the dynamic spiking system. Furthermore, monitoring of possible leaks may be made by rinsing the outside of each syringe after the sampling runs with toluene into a sample vial. This sample can be held for analysis if low dynamic spike recoveries are encountered.

4.3.4 Distribution of Spiked and Native Dioxins and Furans in the Sampling Trains

Figure 3 presents the distribution of the dynamically spiked components and native dioxins and furans collected during all of the runs for this phase. The bars represent the overall average of all compounds collected in all sampling trains for each separate component of the MM5 trains. For runs 28 to 33, the distribution of spiked components and for the native dioxins and furans for the inlet sampling locations is essentially the same, with the distribution heavily favoring the filter assembly. The distribution in the outlet sampling trains for the spiked compounds and for the natives is also very similar, but in this case, the distribution favored the filter assembly and the XAD-2 trap almost equally.

TABLE 7. RECOVERIES OF COMPOUNDS DYNAMICALLY SPIKED AT 100 ng AT THE OUTLET SAMPLING LOCATION DURING RUNS 30 TO 33[a]

Run	Spike level (ng)	^{13}C-labeled analyte	Stack location	Outlet % recovery				
				Cyclone/ filter	Probe/ front half	Back half	XAD	Sum of recovery
30	100	HxCDF	4	28.8	6.53	15.5	72.8	124
		OCDF	4	64.0	6.92	8.70	22.1	102
		TCDD	4	16.8	4.08	4.94	87.2	113
		HxCDD	4	33.9	5.72	11.0	54.7	105
		OCDD	4	79.0	9.34	7.92	21.9	118
31	100	HxCDF	4	14.7	2.44	47.6	61.8	127
		OCDF	4	35.9	4.35	20.2	26.7	87.2
		TCDD	4	9.75	2.17	18.2	83.8	114
		HxCDD	4	15.7	2.18	27.0	53.9	98.8
		OCDD	4	44.9	4.94	20.4	31.3	102
32	100	HxCDF	3	66.8	4.70	7.77	53.5	133
			4	32.6	5.48	21.8	44.9	105
			Average	49.7	5.09	14.8	49.2	119
			RPD[b]	69%	15%	95%	18%	24%[c]
		OCDF	3	98.6	3.92	3.80	14.7	121
			4	62.9	9.03	10.5	14.5	96.9
			Average	80.7	6.48	7.15	14.6	109
			RPD	44%	79%	94%	1%	22%
		TCDD	3	33.5	4.40	2.72	56.7	97.3
			4	26.4	3.38	17.1	65.6	113
			Average	30.0	3.89	9.92	61.2	105
			RPD	24%	26%	145%	15%	14%
		HxCDD	3	70.2	3.86	5.22	32.7	112
			4	38.0	5.40	16.0	42.4	102
			Average	54.1	4.63	10.6	37.5	107
			RPD	60%	33%	102%	26%	10%

(continued)

TABLE 7 (continued)

Run	Spike level (ng)	^{13}C-labeled analyte	Stack location	Outlet % recovery: Cyclone/ filter	Probe/ front half	Back half	XAD	Sum of recovery
32 (continued)		OCDD	3	113	4.16	3.63	15.7	136
			4	76.1	10.8	11.8	18.8	117
			Average	94.5	7.47	7.70	17.3	127
			RPD	39%	89%	106%	18%	15%
33	100	HxCDF	3	63.3	14.6	7.33	33.0	118
			4	67.1	13.5	13.6	22.8	117
			Average	65.2	14.0	10.4	27.9	118
			RPD	6%	7%	60%	37%	1%
		OCDF	3	82.1	18.9	1.94	6.49	109
			4	82.2	13.7	4.38	7.16	107
			Average	82.1	16.3	3.16	6.83	108
			RPD	0%	32%	77%	10%	2%
		TCDD	3	40.1	11.1	3.51	55.3	110
			4	49.1	9.28	6.92	51.8	117
			Average	44.6	10.2	5.22	53.5	114
			RPD	20%	17%	65%	6%	6%
	100	HxCDD	3	62.9	12.7	4.28	22.2	102
			4	66.9	10.7	7.58	19.5	105
			Average	64.9	11.7	5.93	20.9	103
			RPD	6%	18%	56%	13%	2%
		OCDD	3	87.4	21.4	1.42	7.34	118
			4	87.9	16.2	4.37	9.27	118
			Average	87.7	18.8	2.90	8.31	118
			RPD	1%	28%	102%	23%	0%

[a] Only runs 30 and 31 (single train) and 32 and 33 (both trains) were dynamically spiked at the low spiking level.

[b] RPD (relative percent different) = $\frac{\text{Value 1 - Value 2}}{\text{Average of values 1 and 2}}$

[c] The RPD value under the sum of recovery column is relative to the sum of recovery values for each individual train.

TABLE 8. MASS OF NATIVE PCDD/F RECOVERED--RUN 28

Analyte	Inlet						Outlet					
	Stack location	Cyclone/ filter (ng)	Front[a] half (ng)	Back half (ng)	XAD (ng)	Sum of recovery (ng)	Stack location	Cyclone/ filter (ng)	Front[a] half (ng)	Back half (ng)	XAD (ng)	Sum of recovery (ng)
2,3,7,8-TCDF	1	32.9	15.5	1.34	15.7	65.4	3	17.5	3.91	3.84	35.3	60.6
	2	36.2	12.9	1.09	12.7	62.9	4	20.9	3.88	2.8	36.4	64
	Average	34.6	14.2	1.22	14.2	64.2	Average	19.2	3.9	3.32	35.9	62.3
	RPD	10%	18%	20%	21%	4%	RPD	18%	1%	31%	3%	5%
2,3,7,8-TCDD	1	3.43	0.581	0.0663	1.41	5.49	3	0.976	0.149	0.164	2.34	3.63
	2	2.6	0.558	0.035	1.67	4.86	4	0.939	0.178	0.111	2.56	3.79
	Average	3.02	0.57	0.0507	1.54	5.18	Average	0.958	0.164	0.138	2.45	3.71
	RPD	27%	4%	62%	17%	12%	RPD	4%	18%	38%	9%	4%
1,2,3,7,8-PeCDF	1	17.7	5.11	0.495	6.97	30.3	3	7.85	1.49	1.49	15.5	26.3
	2	18.4	5.03	0.256	7.6	31.3	4	8.31	1.69	0.917	15.7	26.6
	Average	18.1	5.07	0.376	7.29	30.8	Average	8.08	1.59	1.2	15.6	26.5
	RPD	4%	2%	64%	9%	3%	RPD	6%	13%	48%	1%	1%
1,2,3,7,8-PeCDD	1	9.42	1.68	0.0927	1.33	12.5	3	2.5	0.496	0.346	4.13	7.47
	2	7.58	1.81	0.051	1.93	11.4	4	2.56	0.523	0.215	4.12	7.42
	Average	8.5	1.75	0.0719	1.63	11.9	Average	2.53	0.51	0.281	4.13	7.45
	RPD	22%	7%	58%	37%	9%	RPD	2%	5%	47%	0%	1%
Total tetra-CDF	1	302	106	12.8	156	577	3	142	22.6	28.6	298	491
	2	315	86.1	9.6	130	541	4	148	25.4	19.6	316	509
	Average	309	96.1	11.2	143	559	Average	145	24	24.1	307	500
	RPD	4%	21%	29%	18%	6%	RPD	4%	12%	37%	6%	4%
Total penta-CDF	1	229	57.1	6.33	87.2	380	3	74.2	17.4	17	135	244
	2	184	57.2	3.8	31.2	276	4	75.2	17.9	11.7	157	262
	Average	207	57.2	5.07	59.2	328	Average	74.7	17.7	14.4	146	253
	RPD	22%	0%	50%	95%	32%	RPD	1%	3%	37%	15%	7%
Total hexa-CDF	1	237	36.4	3.31	64.2	341	3	54.5	11.8	14.7	121	202
	2	234	39.5	1.59	50.1	325	4	67.6	15.1	9.76	136	228
	Average	236	38	2.45	37.2	333	Average	61.1	13.5	12.2	129	215
	RPD	1%	8%	70%	25%	5%	RPD	21%	24%	40%	12%	12%
Total hepta-CDF	1	73	14.4	0.743	8.41	96.6	3	23.6	6.69	20.3	38.2	88.8
	2	71.5	13.8	0.275	9.2	94.8	4	29.9	7.94	3.08	40.6	81.5
	Average	72.3	14.1	0.509	8.81	95.7	Average	26.8	7.32	11.7	39.4	85.2
	RPD	2%	4%	92%	9%	2%	RPD	24%	17%	147%	6%	9%

(continued)

TABLE 8 (continued)

Analyte	Inlet Stack location	Cyclone/ filter (ng)	Front[a] half (ng)	Back half (ng)	XAD (ng)	Sum of recovery (ng)	Outlet Stack location	Cyclone/ filter (ng)	Front[a] half (ng)	Back half (ng)	XAD (ng)	Sum of recovery (ng)
Total octa-CDF	1	14.7	2.16	0.0641	0.425	17.3	3	7.03	1.65	0.594	4.49	13.8
	2	13.2	1.66	0.0304	0.48	15.4	4	7.32	1.93	0.365	4.01	13.6
	Average	14	1.91	0.0473	0.453	16.4	Average	7.18	1.79	0.48	4.25	13.7
	RPD	11%	26%	71%	12%	12%	RPD	4%	16%	48%	11%	1%
Total tetra-CDD	1	81.8	18.5	2.1	52.5	155	3	33.5	5.27	4.05	62.5	105
	2	59.1	19.5	1.61	65.8	146	4	28.5	5.23	3.06	59.1	95.9
	Average	70.5	19	1.86	59.2	150	Average	31	5.25	3.56	60.8	101
	RPD	32%	5%	26%	22%	6%	RPD	16%	1%	28%	6%	9%
Total penta-CDD	1	114	26.6	1.62	34.3	177	3	41.6	7.06	4.89	49.9	103
	2	96.5	30.9	0.932	25.5	154	4	42	7.39	3.3	58.4	111
	Average	105	28.8	1.28	29.9	165	Average	41.8	7.23	4.1	54.2	107
	RPD	17%	15%	54%	29%	14%	RPD	1%	5%	39%	16%	7%
Total hexa-CDD	1	196	34.8	0.97	21.8	254	3	53.8	8.75	6.36	63.5	132
	2	157	44.8	0.745	22.2	225	4	57.9	9.55	3.92	70.3	142
	Average	177	39.8	0.858	22	239	Average	55.9	9.15	5.14	66.9	137
	RPD	22%	25%	26%	2%	12%	RPD	7%	9%	47%	10%	7%
Total hepta-CDD	1	141	47.9	0.574	6.96	196	3	40	12.8	5.35	49.4	108
	2	123	54.9	0.232	7.73	186	4	57.6	13.4	3.17	49.7	124
	Average	132	51.4	0.403	7.35	191	Average	48.8	13.1	4.26	49.6	116
	RPD	14%	14%	85%	10%	5%	RPD	36%	5%	51%	1%	14%
Total octa-CDD	1	85	26.1	0.19	1.23	113	3	25.1	8.96	2.13	16.7	52.9
	2	73.3	26.9	0.117	1.64	102	4	31	9.52	1.26	14.2	56
	Average	79.2	26.5	0.154	1.44	107	Average	28.1	9.24	1.7	15.5	54.4
	RPD	15%	3%	47%	28%	10%	RPD	21%	6%	51%	16%	6%

[a] Front-half rinse includes the probe rinse.

TABLE 9. MASS OF NATIVE PCDD/F RECOVERED--RUN 29

	Inlet						Outlet					
Analyte	Stack location	Cyclone/ filter (ng)	Front[a] half (ng)	Back half (ng)	XAD (ng)	Sum of recovery (ng)	Stack location	Cyclone/ filter (ng)	Front[a] half (ng)	Back half (ng)	XAD (ng)	Sum of recovery (ng)
2,3,7,8-TCDF	1	18.8	4.89	0.0941	2.19	26	3	8.62	0.152	0.969	10.6	20.3
	2	14.6	8.37	0.11	2.95	26	4	10.6	4.46	1.04	8.24	24.3
	Average	16.7	6.63	0.102	2.57	26	Average	9.61	2.31	1	9.42	22.3
	RPD	25%	52%	16%	30%	0%	RPD	21%	186%	7%	25%	18%
2,3,7,8-TCDD	1	1.12	0.208	0.0055	0.097	1.43	3	0.31	0.118	0.0525	0.5	0.981
	2	0.778	0.429	0.0094	0.127	1.34	4	0.468	0.234	0.046	0.374	1.12
	Average	0.949	0.319	0.0074	0.112	1.39	Average	0.389	0.176	0.0493	0.437	1.05
	RPD	36%	69%	52%	27%	6%	RPD	41%	66%	13%	29%	13%
1,2,3,7,8-PeCDF	1	10.4	1.8	0.037	0.758	13	3	3.29	0.961	0.654	2.72	7.63
	2	7	3.17	0.121	0.964	11.3	4	4.13	1.33	0.582	2.05	8.09
	Average	8.7	2.49	0.079	0.861	12.1	Average	3.71	1.15	0.618	2.39	7.86
	RPD	39%	55%	106%	24%	14%	RPD	23%	32%	12%	28%	6%
1,2,3,7,8-PeCDD	1	3.34	0.598	0.0123	0.144	4.09	3	0.877	0.29	0.131	0.719	2.02
	2	2.32	0.964	0.0224	0.225	3.53	4	1.05	0.416	0.131	0.517	2.11
	Average	2.83	0.781	0.0174	0.185	3.81	Average	0.964	0.353	0.131	0.618	2.07
	RPD	36%	47%	58%	44%	15%	RPD	18%	36%	0%	33%	4%
Total tetra-CDF	1	138	36.6	0.745	20.5	196	3	56.2	20.9	8.83	82.7	169
	2	111	66.7	0.753	25.4	204	4	68.6	34.2	8.64	71.7	183
	Average	125	51.7	0.749	23	200	Average	62.4	27.6	8.74	77.2	176
	RPD	22%	58%	1%	21%	4%	RPD	20%	48%	2%	14%	8%
Total penta-CDF	1	105	18.7	0.501	8.48	133	3	38.3	10.9	8.12	33.4	90.7
	2	65.6	33.6	0.67	11.7	112	4	46.5	17.5	7.26	23	94.3
	Average	85.3	26.2	0.586	10.1	122	Average	42.4	14.2	7.69	28.2	92.5
	RPD	46%	57%	29%	32%	17%	RPD	19%	46%	11%	37%	4%
Total hexa-CDF	1	124	11.5	0.326	4.61	140	3	38.7	7.51	5.43	19.6	71.2
	2	118	23.7	0.753	6.27	149	4	51.3	13.4	3.97	13.2	81.9
	Average	121	17.6	0.54	5.44	145	Average	45	10.5	4.7	16.4	76.6
	RPD	5%	69%	79%	31%	6%	RPD	28%	56%	31%	39%	14%
Total hepta-CDF	1	41.8	5.52	0.116	0.906	48.3	3	17.3	4.59	2.05	6.8	30.7
	2	37.3	8.87	0.246	1.32	47.7	4	18.9	6.62	1.45	3.72	30.7
	Average	39.6	7.2	0.181	1.11	48	Average	18.1	5.61	1.75	5.26	30.7
	RPD	11%	47%	72%	37%	1%	RPD	9%	36%	34%	59%	0%

(continued)

TABLE 9 (continued)

Analyte	Inlet Stack location	Cyclone/ filter (ng)	Front[a] half (ng)	Back half (ng)	XAD (ng)	Sum of recovery (ng)	Outlet Stack location	Cyclone/ filter (ng)	Front[a] half (ng)	Back half (ng)	XAD (ng)	Sum of recovery (ng)
Total octa-CDF	1	8.72	1.23	0.0233	0.0762	10	3	3.75	1.48	0.272	0.876	6.38
	2	6.71	1.58	0.0196	0.097	8.41	4	4.26	1.99	0.195	0.326	6.77
	Average	7.72	1.41	0.0215	0.0866	9.23	Average	4.01	1.74	0.234	0.601	6.57
	RPD	26%	25%	17%	24%	17%	RPD	13%	29%	33%	92%	6%
Total tetra-CDD	1	24.1	6.29	0.083	3.5	34	3	11.3	4.01	1.44	10.2	27
	2	18.8	13.1	0.0969	4.35	36.3	4	14.3	7.57	0.876	6.38	29.1
	Average	21.5	9.7	0.09	3.93	35.2	Average	12.8	5.79	1.16	8.29	28
	RPD	25%	70%	15%	22%	7%	RPD	23%	61%	49%	46%	8%
Total penta-CDD	1	44.9	8.78	0.0759	1.91	55.7	3	16.3	4.97	1.78	9.16	32.2
	2	30	16.7	0.209	2.62	49.5	4	18.7	6.86	1.6	6.12	33.3
	Average	37.5	12.7	0.142	2.27	52.6	Average	17.5	5.92	1.69	7.64	32.7
	RPD	40%	62%	94%	31%	12%	RPD	14%	32%	11%	40%	3%
Total hexa-CDD	1	128	11.1	0.14	1.86	141	3	32.6	6.65	1.95	10.7	51.9
	2	75.1	24	0.351	3.32	103	4	39.2	10.6	1.96	7.1	58.9
	Average	102	17.6	0.246	2.59	122	Average	35.9	8.63	1.96	8.9	55.4
	RPD	52%	73%	86%	56%	31%	RPD	18%	46%	1%	40%	13%
Total hepta-CDD	1	84.9	15.6	0.113	0.839	101	3	31.3	10.1	2.1	8.77	52.3
	2	70.2	27.8	0.224	1.3	99.5	4	37.5	14.5	1.58	5.08	58.7
	Average	77.6	21.7	0.169	1.07	100	Average	34.4	12.3	1.84	6.93	55.5
	RPD	19%	56%	66%	43%	2%	RPD	18%	36%	28%	53%	12%
Total octa-CDD	1	46.4	9.32	0.0959	0.24	56.1	3	14.3	8.14	0.269	3.37	26.1
	2	35.7	13.4	0.112	0.376	49.6	4	18.7	9.56	0.823	1.63	30.7
	Average	41.1	11.4	0.104	0.308	52.8	Average	16.5	8.85	0.546	2.5	28.4
	RPD	26%	36%	15%	44%	12%	RPD	27%	16%	101%	70%	16%

[a] Front-half rinse includes the probe rinse.

TABLE 10. MASS OF NATIVE PCDD/F RECOVERED--RUN 30

	Inlet						Outlet					
Analyte	Stack location	Cyclone/ filter (ng)	Front[a] half (ng)	Back half (ng)	XAD (ng)	Sum of recovery (ng)	Stack location	Cyclone/ filter (ng)	Front[a] half (ng)	Back half (ng)	XAD (ng)	Sum of recovery (ng)
2,3,7,8-TCDF	1	18.5	6.38	0.622	2.59	28.1	3	4.71	1.81	2.37	14.8	23.7
	2	12.7	4.79	0.217	4	21.7	4	4.35	2.28	1.09	15	22.7
	Average	15.6	5.59	0.42	3.3	24.9	Average	4.53	2.05	1.73	14.9	23.2
	RPD	37%	28%	96%	43%	26%	RPD	8%	23%	74%	1%	4%
2,3,7,8-TCDD	1	1.46	0.579	0.0243	0.16	2.22	3	0.245	0.077	0.154	0.85	1.33
	2	0.537	0.233	0.051	0.16	0.981	4	0.205	0.0906	0.081	0.67	1.05
	Average	0.999	0.406	0.0377	0.16	1.6	Average	0.225	0.0838	0.118	0.76	1.19
	RPD	92%	85%	71%	0%	77%	RPD	18%	16%	62%	24%	24%
1,2,3,7,8-PeCDF	1	10.7	2.73	0.23	0.866	14.5	3	2.24	0.721	1.93	5.47	10.4
	2	5.37	2.19	0.147	1.51	9.21	4	2.49	1.08	0.849	5.9	10.3
	Average	8.03	2 46	0.189	1.19	11.9	Average	2.36	0.901	1.39	5.69	10.3
	RPD	66%	22%	44%	54%	44%	RPD	11%	40%	78%	8%	1%
1,2,3,7,8-PeCDD	1	3.1	0.843	0.056	0.17	4.17	3	0.674	0.237	0.425	1.29	2.63
	2	1.15	0.532	0.1	0.26	2.05	4	0.664	0.331	0.142	1.28	2.42
	Average	2.13	0.688	0.078	0.215	3.11	Average	0.669	0.284	0.284	1.29	2.52
	RPD	92%	45%	56%	42%	68%	RPD	1%	33%	100%	1%	8%
Total tetra-CDF	1	158	43.6	3.91	23.7	229	3	31.7	10.4	18.2	115	175
	2	106	33.5	1.99	39.3	181	4	33.1	17.3	9.58	142	202
	Average	132	38.6	2.95	31.5	205	Average	32.4	13.9	13.9	129	189
	RPD	39%	26%	65%	50%	23%	RPD	4%	50%	62%	21%	14%
Total penta-CDF	1	103	28.9	2.49	10.5	145	3	23.7	8.05	21.2	55.8	109
	2	57.2	26.9	1.93	18.8	105	4	28.6	12.3	10.2	70.9	122
	Average	80.1	27.9	2.21	14.7	125	Average	26.1	10.2	15.7	63.4	115
	RPD	57%	7%	25%	56%	32%	RPD	19%	42%	70%	24%	11%
Total hexa-CDF	1	83	39.8	1.79	4.66	129	3	27.2	8.12	14.7	34.8	84.8
	2	58.1	36.8	2.36	9.56	107	4	40.2	20.2	8.3	42	111
	Average	70.6	38.3	2.08	7.11	118	Average	33.7	14.2	11.5	38.4	97.8
	RPD	35%	8%	27%	69%	19%	RPD	39%	85%	56%	19%	27%
Total hepta-CDF	1	39	12.2	0.437	1.06	52.7	3	18.2	5.12	5.47	12.2	41
	2	23.2	10.9	0.42	1.91	36.4	4	17.5	9.65	3.2	12.9	43.2
	Average	31.1	11.6	0.429	1.49	44.6	Average	17.8	7.39	4.34	12.6	42.1
	RPD	51%	11%	4%	57%	37%	RPD	4%	61%	52%	6%	5%

(continued)

TABLE 10 (continued)

Analyte	Inlet Stack location	Cyclone/ filter (ng)	Front[a] half (ng)	Back half (ng)	XAD (ng)	Sum of recovery (ng)	Outlet Stack location	Cyclone/ filter (ng)	Front[a] half (ng)	Back half (ng)	XAD (ng)	Sum of recovery (ng)
Total octa-CDF	1	16.4	2.04	0.0604	0.097	18.6	3	7.85	2.16	0.806	1.81	12.6
	2	6.34	2.06	0.12	0.18	8.7	4	5.62	2.1	0.502	1.81	10
	Average	11.4	2.05	0.0902	0.139	13.6	Average	6.73	2.13	0.654	1.81	11.3
	RPD	88%	1%	66%	60%	73%	RPD	33%	3%	46%	0%	23%
Total tetra-CDD	1	36	8.25	0.6	3.74	48.6	3	6.16	2.67	2.9	17.5	29.2
	2	15.3	5.02	0.3	4	24.6	4	5.51	2.63	1	16.4	25.5
	Average	25.7	6.64	0.45	3.87	36.6	Average	5.84	2.65	1.95	17	27.4
	RPD	81%	49%	67%	7%	66%	RPD	11%	2%	97%	6%	14%
Total penta-CDD	1	38	13	0.582	1.67	53.3	3	11.3	3.79	5.25	14.1	34.4
	2	15.9	7.26	0.312	2.19	25.7	4	9.84	5.14	1.11	14.5	30.6
	Average	27	10.1	0.447	1.93	39.5	Average	10.6	4.47	3.18	14.3	32.5
	RPD	82%	57%	60%	27%	70%	RPD	14%	30%	130%	3%	12%
Total hexa-CDD	1	56	26.2	0.65	1.64	84.5	3	22	6.62	4.65	14.9	48.2
	2	30.6	18.1	0.372	1.71	50.8	4	25.1	14.8	1.76	12.9	54.6
	Average	43.3	22.2	0.511	1.68	67.6	Average	23.6	10.7	3.21	13.9	51.4
	RPD	59%	36%	54%	4%	50%	RPD	13%	76%	90%	14%	12%
Total hepta-CDD	1	71	24.1	0.365	0.849	96.3	3	26	10.7	3.84	11.8	52.3
	2	38.2	14.7	0.065	1.05	54	4	25.5	15.7	1.98	11.6	54.8
	Average	54.6	19.4	0.215	0.95	75.2	Average	25.7	13.2	2.91	11.7	53.5
	RPD	60%	48%	140%	21%	56%	RPD	2%	38%	64%	2%	5%
Total octa-CDD	1	55	11	0.154	0.259	66.4	3	17.4	8.42	1.46	4.73	32
	2	26.9	7.89	0.131	0.134	35.1	4	15	9.85	0.771	4.28	29.9
	Average	41	9.45	0.143	0.197	50.7	Average	16.2	9.14	1.12	4.51	31
	RPD	69%	33%	16%	63%	62%	RPD	15%	16%	62%	10%	7%

[a] Front-half rinse includes the probe rinse.

TABLE 11. MASS OF NATIVE PCDD/F RECOVERED--RUN 31

	Inlet						Outlet					
Analyte	Stack location	Cyclone/ filter (ng)	Front[a] half (ng)	Back half (ng)	XAD (ng)	Sum of recovery (ng)	Stack location	Cyclone/ filter (ng)	Front[a] half (ng)	Back half (ng)	XAD (ng)	Sum of recovery (ng)
2,3,7,8-TCDF	1	13.6	5.84	0.44	5.73	25.6	3	2.28	2.07	0.808	10.6	15.8
	2	11.6	6.45	0.527	4.96	23.5	4	2.41	0.915	3.02	11.2	17.5
	Average	12.6	6.14	0.484	5.34	24.6	Average	2.35	1.49	1.91	10.9	16.7
	RPD	16%	10%	18%	14%	9%	RPD	6%	78%	116%	6%	10%
2,3,7,8-TCDD	1	0.711	0.238	0.031	0.39	1.37	3	0.119	0.12	0.028	0.49	0.757
	2	0.582	0.189	0.035	0.23	1.04	4	0.1	ND	0.171	0.54	0.811
	Average	0.647	0.214	0.033	0.31	1.2	Average	0.11	0.06	0.0995	0.515	0.784
	RPD	20%	23%	12%	52%	28%	RPD	17%	200%	144%	10%	7%
1,2,3,7,8-PeCDF	1	6.51	2.31	0.282	1.91	11	3	1.34	0.83	0.493	4.72	7.38
	2	6.31	2.73	0.257	1.53	10.8	4	0.395	0.647	1.91	3.71	6.66
	Average	6.41	2.52	0.27	1.72	10.9	Average	0.868	0.739	1.2	4.22	7.02
	RPD	3%	17%	9%	22%	2%	RPD	109%	25%	118%	24%	10%
1,2,3,7,8-PeCDD	1	1.45	0.525	0.06	0.28	2.32	3	0.324	0.225	0.103	0.97	1.62
	2	1.38	0.745	0.0552	0.26	2.44	4	1.61	0.112	0.387	0.81	2.92
	Average	1.42	0.635	0.0576	0.27	2.38	Average	0.967	0.169	0.245	0.89	2.27
	RPD	5%	35%	8%	7%	5%	RPD	133%	67%	116%	18%	57%
Total tetra-CDF	1	127	44.6	4.02	55.7	231	3	18.7	15.7	6.41	102	143
	2	83.5	43.3	4.7	47.3	179	4	15.4	6.58	26.6	78.1	127
	Average	105	44	4.36	51.5	205	Average	17.1	11.1	16.5	90.1	135
	RPD	41%	3%	16%	16%	25%	RPD	19%	82%	122%	27%	12%
Total penta-CDF	1	75.3	29.9	3.4	23.2	132	3	15.7	10	6.39	57.1	89.2
	2	65.3	27.3	3.44	19.8	116	4	12.5	4.47	24.9	38.1	80
	Average	70.3	28.6	3.42	21.5	124	Average	14.1	7.24	15.6	47.6	84.6
	RPD	14%	9%	1%	16%	13%	RPD	23%	76%	119%	40%	11%
Total hexa-CDF	1	72.1	43	3.04	15.8	134	3	26.9	14.2	4.68	28.1	73.9
	2	98.5	44.7	2.28	8.76	154	4	13.2	3.4	23	27.9	67.5
	Average	85.3	43.9	2.66	12.3	144	Average	20.1	8.8	13.8	28	70.7
	RPD	31%	4%	29%	57%	14%	RPD	68%	123%	133%	1%	9%
Total hepta-CDF	1	31.1	12.3	0.777	3.17	47.3	3	14.2	7.64	2.41	8.48	32.7
	2	39.2	17.7	0.661	2.18	59.7	4	9.81	2.76	8.46	11.2	32.2
	Average	35.2	15	0.719	2.68	53.5	Average	12	5.2	5.44	9.84	32.5
	RPD	23%	36%	16%	37%	23%	RPD	37%	94%	111%	28%	2%

(continued)

TABLE 11 (continued)

Analyte	Inlet Stack location	Cyclone/ filter (ng)	Front[a] half (ng)	Back half (ng)	XAD (ng)	Sum of recovery (ng)	Outlet Stack location	Cyclone/ filter (ng)	Front[a] half (ng)	Back half (ng)	XAD (ng)	Sum of recovery (ng)
Total octa-CDF	1	9.78	3.17	ND	0.291	13.2	3	5.65	2.32	0.484	2.02	10.5
	2	10.8	3.52	0.0805	0.337	14.7	4	5.17	1.17	1.43	2.1	9.87
	Average	10.3	3.35	0.0403	0.314	14	Average	5.41	1.75	0.957	2.06	10.2
	RPD	10%	10%	200%	15%	11%	RPD	9%	66%	99%	4%	6%
Total tetra-CDD	1	21.4	6.94	0.6	5.48	34.4	3	3.23	2.11	0.5	13.6	19.4
	2	11.1	3.92	0.5	4.48	20	4	3.63	1.13	3.6	10.1	18.5
	Average	16.3	5.43	0.55	4.98	27.2	Average	3.43	1.62	2.05	11.9	19
	RPD	63%	56%	18%	20%	53%	RPD	12%	60%	151%	29%	5%
Total penta-CDD	1	22.4	7.79	0.36	3.26	33.8	3	4.99	3.41	1.1	10.8	20.3
	2	18.5	9.78	0.496	2.77	31.5	4	5.42	2.25	5.2	8.46	21.3
	Average	20.5	8.79	0.428	3.02	32.7	Average	5.21	2.83	3.15	9.63	20.8
	RPD	19%	23%	32%	16%	7%	RPD	8%	41%	130%	24%	5%
Total hexa-CDD	1	22.2	17.3	0.325	2.32	42.1	3	14.3	12.6	1.21	9.29	37.4
	2	41.3	26.9	0.627	2.02	70.8	4	8.13	2.56	6.21	7.81	24.7
	Average	31.8	22.1	0.476	2.17	56.5	Average	11.2	7.58	3.71	8.55	31.1
	RPD	60%	43%	63%	14%	51%	RPD	55%	132%	135%	17%	41%
Total hepta-CDD	1	39.3	14.1	0.318	1.12	54.8	3	15.7	10.2	1.65	9.13	36.7
	2	41.3	21.9	0.372	1.29	64.9	4	11.3	4.03	5.06	9.86	30.3
	Average	40.3	18	0.345	1.21	59.9	Average	13.5	7.12	3.36	9.5	33.5
	RPD	5%	43%	16%	14%	17%	RPD	33%	87%	101%	8%	19%
Total octa-CDD	1	27.7	8.45	0.145	0.435	36.7	3	12.2	7.12	0.96	4.42	24.7
	2	28.3	10.8	0.187	0.517	39.8	4	9.83	3.85	2.33	4.72	20.7
	Average	28	9.63	0.166	0.476	38.3	Average	11	5.49	1.65	4.57	22.7
	RPD	2%	24%	25%	17%	8%	RPD	22%	60%	83%	7%	18%

[a] Front-half rinse includes the probe rinse.

TABLE 12. MASS OF NATIVE PCDD/F RECOVERED--RUN 32

Analyte	Inlet						Outlet					
	Stack location	Cyclone/ filter (ng)	Front[a] half (ng)	Back half (ng)	XAD (ng)	Sum of recovery (ng)	Stack location	Cyclone/ filter (ng)	Front[a] half (ng)	Back half (ng)	XAD (ng)	Sum of recovery (ng)
2,3,7,8-TCDF	1	37.3	11.8	0.129	1.87	51.1	3	7.85	2.48	4.39	8.32	23
	2	24.8	1.43	0.104	1.99	28.3	4	6.22	1.97	1.99	6.69	16.9
	Average	31	6.62	0.117	1.93	39.7	Average	7.04	2.23	3.19	7.51	20
	RPD	40%	157%	21%	6%	57%	RPD	23%	23%	75%	22%	31%
2,3,7,8-TCDD	1	2.17	0.664	0.017	0.14	3	3	0.335	0.128	0.043	0.354	0.86
	2	1.21	0.108	ND	0.108	1.42	4	0.281	0.046	0.141	0.359	0.827
	Average	1.69	0.386	0.0085	0.124	2.21	Average	0.308	0.087	0.092	0.357	0.844
	RPD	57%	144%	200%	26%	71%	RPD	18%	94%	107%	1%	4%
1,2,3,7,8-PeCDF	1	15.7	4.81	0.08	0.68	2.13	3	3.33	0.958	0.332	2.95	7.57
	2	NA	0.712	0.042	0.725	1.48	4	2.04	0.768	1.04	2.34	6.19
	Average	7.86	2.76	0.061	0.703	11.4	Average	2.69	0.863	0.687	2.65	6.88
	RPD	200%	148%	62%	6%	174%	RPD	48%	22%	103%	23%	20%
1,2,3,7,8-PeCDD	1	4.3	1.44	0.032	0.112	5.89	3	0.885	0.212	0.078	0.572	1.75
	2	NA	0.193	0.024	ND	0.217	4	0.447	0.179	0.206	0.512	1.34
	Average	2.15	0.817	0.028	0.056	3.05	Average	0.666	0.196	0.142	0.542	1.55
	RPD	200%	153%	29%	200%	186%	RPD	66%	17%	90%	11%	26%
Total tetra-CDF	1	349	107	0.919	22.2	479	3	66	20.9	4.39	64.6	156
	2	236	14.6	0.816	22.1	274	4	53.7	17	20	75.1	166
	Average	293	60.8	0.868	22.2	376	Average	59.9	18.9	12.2	69.9	161
	RPD	39%	152%	12%	0%	55%	RPD	21%	21%	128%	15%	6%
Total penta-CDF	1	166	49.1	0.777	7.27	223	3	37.3	11.1	2.81	34.6	85.8
	2	NA	7.55	0.827	8.13	16.5	4	23.1	9.28	13.1	29.9	75.4
	Average	83	28.3	0.802	7.7	120	Average	30.2	10.2	7.96	32.3	80.6
	RPD	200%	147%	6%	11%	172%	RPD	47%	18%	129%	15%	13%
Total hexa-CDF	1	135	85.7	1.09	5.05	227	3	60.9	39.9	3.35	26.4	131
	2	91	10.1	0.942	7.27	109	4	17.2	11.3	8.66	23	60.2
	Average	113	47.9	1.01	6.16	168	Average	39.1	25.6	6.01	24.7	95.4
	RPD	39%	158%	15%	36%	70%	RPD	112%	112%	88%	14%	74%
Total hepta-CDF	1	53.6	27.2	0.27	1.37	82.4	3	25.7	6.38	1.21	7.04	40.3
	2	36.4	3.89	0.643	1.88	42.8	4	10.4	5.28	3.71	7.57	27
	Average	45	15.5	0.457	1.63	62.6	Average	18	5.83	2.46	7.31	33.6
	RPD	38%	150%	82%	31%	63%	RPD	85%	19%	102%	7%	40%

(continued)

TABLE 12 (continued)

Analyte	Inlet						Outlet					
	Stack location	Cyclone/ filter (ng)	Front[a] half (ng)	Back half (ng)	XAD (ng)	Sum of recovery (ng)	Stack location	Cyclone/ filter (ng)	Front[a] half (ng)	Back half (ng)	XAD (ng)	Sum of recovery (ng)
Total octa-CDF	1	16.2	4.86	ND	0.199	2.13	3	8.6	1.11	ND	1.12	10.8
	2	8.93	1.01	ND	ND	9.94	4	4.74	1.53	0.837	1.1	8.21
	Average	12.6	2.94	ND	0.0995	15.6	Average	6.67	1.32	0.419	1.11	9.52
	RPD	58%	131%	NA	200%	73%	RPD	58%	32%	200%	2%	27%
Total tetra-CDD	1	62.1	18	0.296	2.7	83.1	3	9.99	2.97	0.577	8.3	21.8
	2	34.2	1.5	0.381	1.81	37.9	4	6	1.67	2.49	9.55	19.7
	Average	48.2	9.75	0.339	2.26	60.5	Average	8	2.32	1.53	8.93	20.8
	RPD	58%	169%	25%	39%	75%	RPD	50%	56%	125%	14%	10%
Total penta-CDD	1	62.4	20.6	0.228	0.712	83.9	3	19.6	3.34	0.578	4.48	28
	2	NA	1.6	0.217	0.76	2.58	4	6.72	2.25	1.9	4.45	15.3
	Average	31.2	11.1	0.223	0.736	43.3	Average	13.2	2.8	1.24	4.47	21.7
	RPD	200%	171%	5%	7%	188%	RPD	98%	39%	107%	1%	59%
Total hexa-CDD	1	112	59.4	0.289	1	173	3	69.3	10.8	0.694	6.83	87.6
	2	60.5	4.39	0.69	1.02	66.6	4	10.9	6.87	1.85	5.52	25.1
	Average	86.3	31.9	0.49	1.01	120	Average	40.1	8.82	1.27	6.18	56.4
	RPD	60%	172%	82%	2%	89%	RPD	146%	45%	91%	21%	111%
Total hepta-CDD	1	122	51.1	0.093	0.597	174	3	49.4	9.23	0.827	6.08	65.5
	2	47.2	3.99	ND	0.8	52	4	16.4	7.85	2.83	6.79	33.9
	Average	84.6	27.5	0.0465	0.699	113	Average	32.9	8.54	1.85	6.44	49.7
	RPD	88%	171%	200%	29%	108%	RPD	100%	16%	109%	11%	64%
Total octa-CDD	1	76.3	22.4	ND	0.222	98.9	3	28.7	4.44	0.493	2.37	36
	2	36.9	3.12	ND	ND	40	4	15.8	5.9	1.48	2.58	25.8
	Average	56.6	12.8		0.111	69.5	Average	22.2	5.17	0.987	2.48	30.9
	RPD	70%	151%	ERR	200%	85%	RPD	58%	28%	100%	8%	33%

[a] Front-half rinse includes the probe rinse.

TABLE 13. MASS OF NATIVE PCDD/F RECOVERED--RUN 33

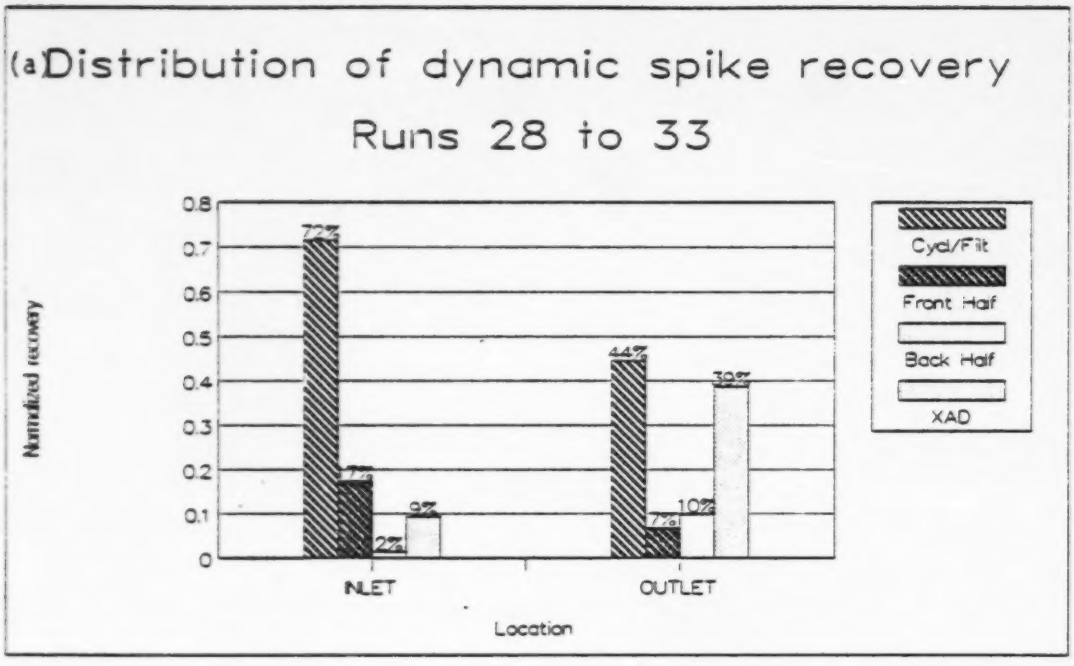
Analyte	Inlet						Outlet					
	Stack location	Cyclone/ filter (ng)	Front[a] half (ng)	Back half (ng)	XAD (ng)	Sum of recovery (ng)	Stack location	Cyclone/ filter (ng)	Front[a] half (ng)	Back half (ng)	XAD (ng)	Sum of recovery (ng)
2,3,7,8-TCDF	1	58	3.49	0.138	4.14	65.8	3	10.5	3.67	0.499	11.3	26
	2	63.5	4.89	0.095	3.55	71.8	4	10.3	4.82	0.993	8.04	24.2
	Average	60.7	4.09	0.117	3.85	68.8	Average	10.4	4.24	0.746	9.67	25.1
	RPD	9%	29%	37%	15%	9%	RPD	2%	27%	66%	34%	7%
2,3,7,8-TCDD	1	4.03	0.267	0.027	0.213	4.54	3	0.545	0.228	0.044	0.594	1.41
	2	4.34	0.442	ND	0.208	4.99	4	0.66	0.299	0.071	0.484	1.51
	Average	4.19	0.355	0.0135	0.211	4.76	Average	0.603	0.264	0.0575	0.539	1.46
	RPD	7%	49%	200%	2%	9%	RPD	19%	27%	47%	20%	7%
1,2,3,7,8-PeCDF	1	21.5	1.67	0.163	1.39	24.7	3	1.53	1.81	0.389	4.37	8.1
	2	22.9	2.77	1.59	1.04	28.3	4	4.28	2.39	0.619	2.7	9.99
	Average	22.2	2.22	0.876	1.22	26.5	Average	2.91	2.1	0.504	3.54	9.05
	RPD	6%	50%	163%	29%	14%	RPD	95%	28%	46%	47%	21%
1,2,3,7,8-PeCDD	1	7.97	0.499	0.046	0.273	8.79	3	1.17	0.51	0.097	0.971	2.75
	2	9.06	0.995	0.277	0.199	10.5	4	1.14	0.585	0.15	0.735	2.61
	Average	8.52	0.747	0.162	0.236	9.66	Average	1.16	0.548	0.124	0.853	2.68
	RPD	13%	66%	143%	31%	18%	RPD	3%	14%	43%	28%	5%
Total tetra-CDF	1	490	20.5	1.3	51.2	563	3	96.9	33.3	4.7	131	266
	2	574	39.8	0.885	38	653	4	95.1	43.1	10	102	250
	Average	532	30.2	1.09	44.6	608	Average	96	38.2	7.35	117	258
	RPD	16%	64%	38%	30%	15%	RPD	2%	26%	72%	25%	6%
Total penta-CDF	1	256	17.2	1.56	17.4	292	3	42.8	21.1	4.24	44.6	113
	2	279	28.9	1.15	12.3	321	4	50.3	23.7	8.66	36.7	119
	Average	268	23.1	1.36	14.9	307	Average	46.6	22.4	6.45	40.7	116
	RPD	9%	51%	30%	34%	9%	RPD	16%	12%	69%	19%	5%
Total hexa-CDF	1	196	21.1	1.9	11.5	230	3	36.1	21.7	4.06	29.2	91.1
	2	207	33.3	1.26	9.46	251	4	37.5	31.2	6.66	17.8	93.2
	Average	202	27.2	1.58	10.5	241	Average	36.8	26.5	5.36	23.5	92.1
	RPD	5%	45%	41%	19%	9%	RPD	4%	36%	49%	49%	2%
Total hepta-CDF	1	70	7.98	0.363	2.13	80.5	3	17.2	8.6	1.29	6.06	33.2
	2	74.9	12.4	0.337	1.94	89.6	4	17.6	11	1.98	4.24	34.8
	Average	72.5	10.2	0.35	2.04	85	Average	17.4	9.8	1.64	5.15	34
	RPD	7%	43%	7%	9%	11%	RPD	2%	24%	42%	35%	5%

(continued)

TABLE 13 (continued)

Analyte	Inlet Stack location	Cyclone/ filter (ng)	Front[a] half (ng)	Back half (ng)	XAD (ng)	Sum of recovery (ng)	Outlet Stack location	Cyclone/ filter (ng)	Front[a] half (ng)	Back half (ng)	XAD (ng)	Sum of recovery (ng)
Total octa-CDF	1	18	2.05	ND	0.305	20.4	3	6.16	2.23	0.228	0.874	9.49
	2	21.1	2.85	ND	0.345	24.3	4	6.01	2.69	0.342	0.804	9.85
	Average	19.6	2.45	ND	0.325	22.3	Average	6.09	2.46	0.285	0.839	9.67
	RPD	16%	33%	NA	12%	17%	RPD	2%	19%	40%	8%	4%
Total tetra-CDD	1	121	4.18	1.7	7.05	134	3	14.9	6.12	0.758	20.2	42
	2	129	10	0.182	4.46	144	4	16.3	7.4	1.44	17.3	42.4
	Average	125	7.09	0.942	5.76	139	Average	15.6	6.76	1.1	18.8	42.2
	RPD	6%	82%	161%	45%	7%	RPD	9%	19%	62%	15%	1%
Total penta-CDD	1	115	6.17	0.401	2.31	124	3	17.6	6.97	0.991	10.6	36.2
	2	129	11.7	0.277	2.2	143	4	18.2	9.34	2.12	7.25	36.9
	Average	122	8.94	0.339	2.26	134	Average	17.9	8.16	1.56	8.93	36.5
	RPD	11%	62%	37%	5%	14%	RPD	3%	29%	72%	38%	2%
Total hexa-CDD	1	169	12.4	0.553	2.96	185	3	16.2	7.99	1.07	8.71	34
	2	197	23.9	0.373	2.02	223	4	16.1	19.7	1.75	5.35	42.9
	Average	183	18.2	0.463	2.49	204	Average	16.2	13.8	1.41	7.03	38.4
	RPD	15%	63%	39%	38%	19%	RPD	1%	85%	48%	48%	23%
Total hepta-CDD	1	145	11.3	0.284	1.04	158	3	25.3	12.9	0.755	5.25	44.2
	2	170	19.7	0.134	0.919	191	4	27	17.2	1.42	4	49.6
	Average	158	15.5	0.209	0.98	174	Average	26.2	15.1	1.09	4.63	46.9
	RPD	16%	54%	72%	12%	19%	RPD	6%	28%	61%	27%	12%
Total octa-CDD	1	85	6.84	ND	0.561	92.4	3	18.8	8.12	0.419	1.98	29.3
	2	91.8	12.5	0.238	0.528	105	4	18.4	9.36	0.599	1.87	30.2
	Average	88.4	9.67	0.119	0.545	98.7	Average	18.6	8.74	0.509	1.93	29.8
	RPD	8%	59%	200%	6%	13%	RPD	2%	14%	35%	6%	3%

[a] Front-half rinse includes the probe rinse.



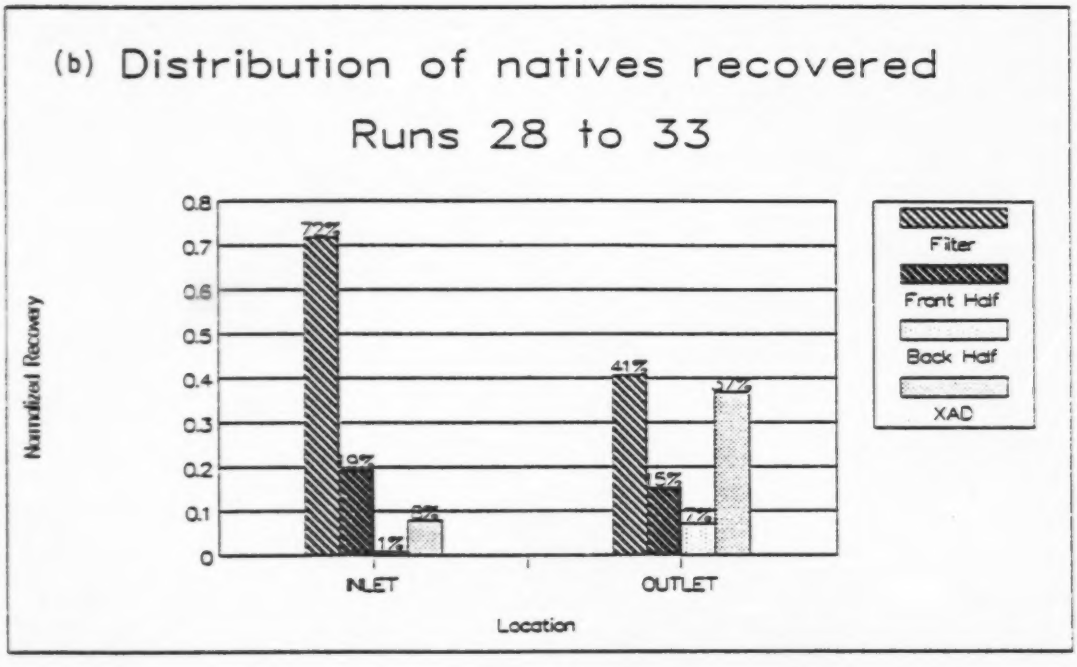


Figure 3. Distribution of (a) dynamic spikes and (b) native PCDD/PCDFs in MM5 sampling trains recovered during runs 28 to 33.

This is expected, since particulate loading at the outlet sampling port is decreased, thereby allowing compounds in the vapor phase to break through to the back part of the sampling train. However, based on the high percentage of compounds captured in the filter assembly, it appears that particulate loading at the outlet was relatively high as compared to earlier studies for this set of sampling runs.

As a point of comparison, a similar plot was prepared for runs 18 to 21 from data previously reported[4] (Figure 4). This set of runs was conducted using sampling trains whose back-half component was coated with Apiezon-L grease to enhance recovery from the glassware. The distribution of the spiked and native compounds for the inlet sampling trains for this set of runs is very similar to those presented in Figure 3 (runs 28 to 33). However, the compound distribution for the outlet sampling trains is different. For runs 18 to 21, the distribution in the outlet sampling trains favored the back-half glassware with little contribution from the filter assembly, whereas for runs 28 to 33, the distribution favors the filter assembly and XAD-2 trap, with minimal contribution from the back-half glassware. This could be related to two distinct factors, which given the data available, cannot be separated. The first factor is particulate loading differences between the two sets of runs. It appears that for runs 28 to 33, the electrostatic precipitator was either not functioning properly, or was overwhelmed by extremely high particulate loading levels. The second factor is the use of Apiezon-L to coat the back-half glassware for runs 18 to 21. The sampling trains for runs 28 to 33 did not have the Apiezon-L coating. It would appear more likely that particulate loading would have had the most effect, but given the lack of supporting data, this aspect remains in doubt.

Particulate material in the flue sorbs the gas phase dioxins and furans (native or spiked) when it impinges on the filter assembly, thereby effectively trapping these compounds in the filter assembly of the MM5 sampling train. As was discussed in a previous report,[5] increasing the temperature of the filter assembly reduced the adsorptivity of the dynamically spiked components but not of the native dioxins and furans. Since particulate loading data were not collected during any of the test runs, the differential effects of Apiezon-L coatings and of particulate loading cannot be differentiated for these sets of runs.

4.4 STATISTICAL ANALYSIS

A number of analysis of variance models were run on the data presented in the preceding sections of this report. The variables used in the conduct of these tests were run number (demonstrative of day-to-day variations), dynamic spike level, sampling location, replicate recoveries, and specific dynamically spiked compounds. Several analysis of variance models were considered and after each model, the factors or combinations of factors which did not have a significant effect on the result were removed and an additional model fitted.

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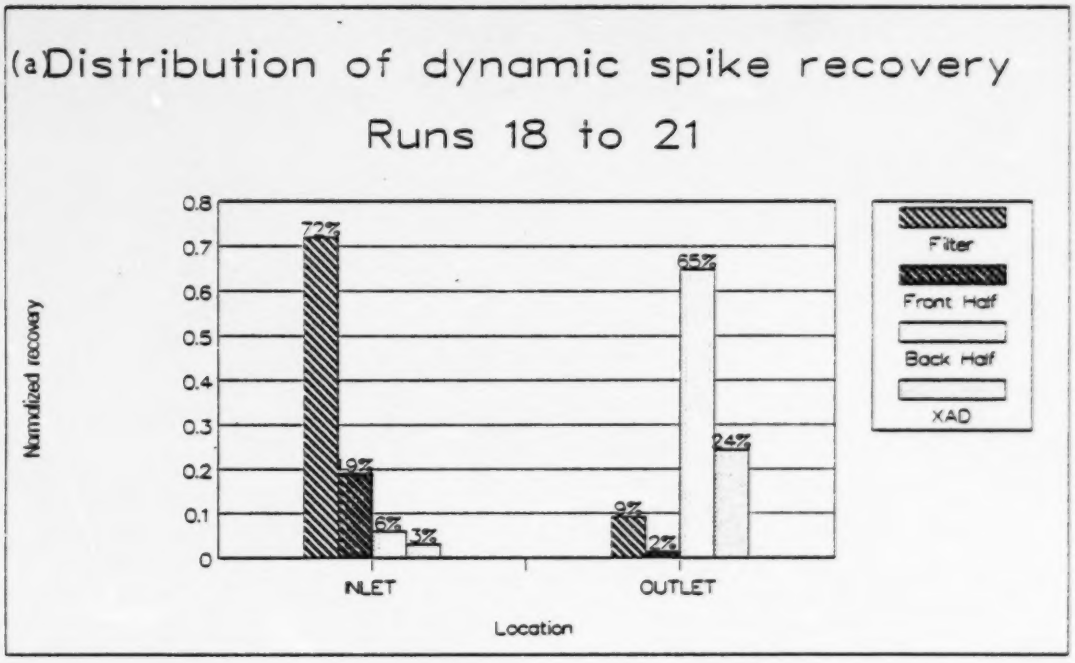
[4] MRI. 1989. op. cit.
[5] MRI. 1989. op. cit.



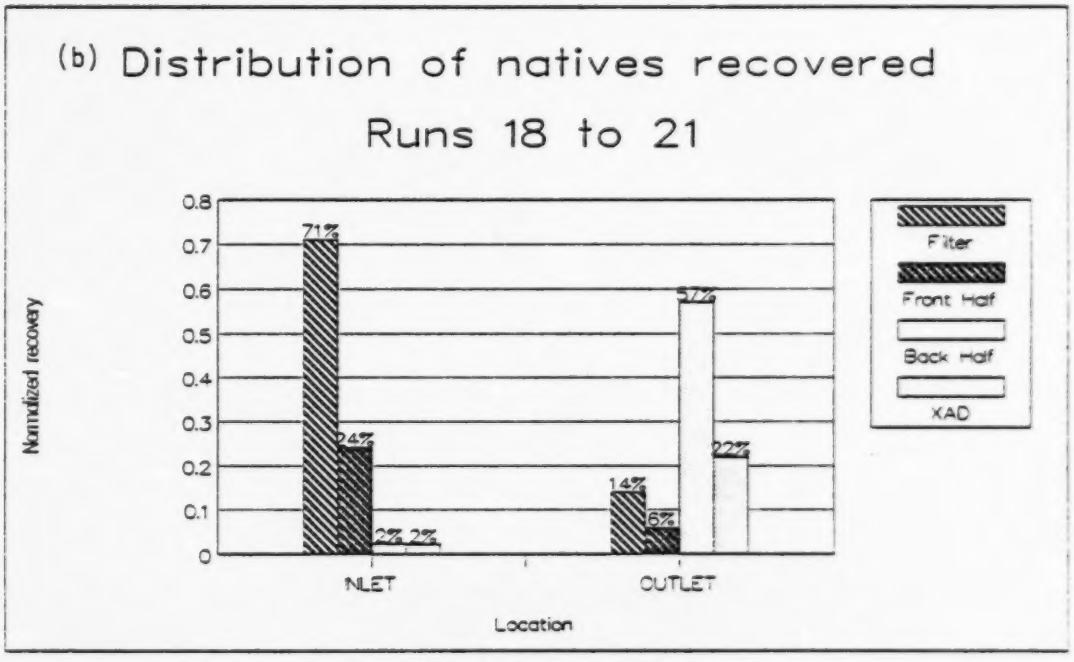


Figure 4. Distribution of (a) dynamic spikes and (b) native PCDD/PCDFs in MM5 sampling trains recovered during runs 18 to 21.

4.4.1 Evaluation of Sampling and Analysis Precision

Tables 14 and 15 present the results of the analysis of variance model that best fit the results generated during this study for sampling precision of the MM5 train. To test the null hypothesis that the MM5 sampling trains produced precise results, the spike recovery was used as the dependent variable. Differences between replicate sampling trains were found to be nonsignificant.

The factors that were found to influence sampling precision the most were run number (i.e., day-to-day variability), sampling location (i.e., inlet or outlet), the dynamically spiked compound, and the interaction between run and sampling location. None of these were unexpected, and in general terms indicate that for any given day, a pair of MM5 sampling trains sampling a particular portion of a stack effluent for any given compound will produce results of acceptable precision.

Sampling location had the most effect on recovery, whereas the other three variables had effects of a similar magnitude. This can be discerned from the magnitude of the F-ratio in Table 14. Because the experimental design was not totally balanced, the sums of squares are not additive, but the magnitude of the F-ratio provides an indication of the relative effect of the variables tested. All of these variables produced statistically significant differences, with P-values ranging from zero to three decimal places, and accounted for 74% of the variability observed.

The difference between the aggregate of all replicate runs (same spiking level at the same sampling location) was not significant ($P = 0.103$). This also applies to all but one of all individual replicate runs. Replicate samples collected during run 29 at the inlet sampling location exhibited significant differences. The reasons for this have been discussed elsewhere in this report.

Seven pairs of runs (runs 28--inlet and outlet, run 29--outlet only, and runs 32 and 33--inlet and outlet) were used to estimate the precision of the dynamic spike sampling and analysis for each compound. This is expressed as the pooled standard deviation of the difference in recovery between each set of replicates:

- ^{13}C-HxCDF 12.3%
- ^{13}C-OCDF 7.01%
- ^{13}C-TCDD 8.27%
- ^{13}C-HxCDD 7.18%
- ^{13}C-OCDD 5.77%

Thus, for ^{13}C-HxCDF, the difference between replicate sampling trains is estimated to have a standard deviation of 12.3% recovery. Values would be expected to replicate to within 12.3% about two-thirds of the time.

TABLE 14. ANALYSIS OF VARIANCE RESULTS USING DYNAMIC SPIKE RECOVERY AS THE DEPENDENT VARIABLE

Source of variation	Sum of squares	DF	Mean of squares	F-ratio	P
Run number	13,659.423	5	2,731.885	15.002	0.000
Sampling location	23,592.856	1	23,592.856	129.557	0.000
Compound	5,695.963	4	1,423.991	7.820	0.000
Run number and sampling location interaction	10,469.645	5	2,093.929	11.499	0.000
Error	18,938.806	104	182.104		
Standard deviation		13.5			
Squared multiple R		0.738			

TABLE 15. NET EFFECTS OF SOURCES OF VARIATION ON DYNAMIC SPIKE RECOVERIES USING ANALYSIS OF VARIANCE MODEL

	Net effect on recovery (%)	Predicted recovery (%)
Predicted recovery (no variability)		101
Day-to-day variability		
Day 1	+11.2	112
Day 2	-6.90	93.9
Day 3	+1.40	102
Day 4	+16.1	117
Day 5	-13.3	87.4
Day 6	+8.46	109
Sampling location		
Inlet	-14.0	86.7
Outlet	+14.0	115
Compound		
^{13}-HxCDF	+9.36	110
^{13}-OCDF	-6.03	94.7
^{13}-TCDD	+3.55	104
^{13}-HxCDD	-9.65	91.1
^{13}-OCDD	-2.77	99.0
Day-sampling location interaction		
Day 1, inlet	+14.5	115
Day 1, outlet	-14.5	86.2
Day 2, inlet	-8.13	92.6
Day 2, outlet	+8.13	109
Day 3, inlet	+3.48	104
Day 3, outlet	-3.48	97.3
Day 4, inlet	+7.68	109
Day 4, outlet	-7.68	93.0
Day 5, inlet	-11.9	88.9
Day 5, outlet	+11.9	113
Day 6, inlet	+5.78	107
Day 6, outlet	-5.78	95.0

4.4.2 Evaluation of Sampling and Analysis Accuracy

Using the absolute difference between the dynamic spike recoveries and 100% as the dependent variable, the best analysis of variance model indicated that run number, sampling location, replication, and the interaction between run and sampling location significantly affected the results (Tables 16 and 17). This accounted for the variability in 40% of the measurements. The variability in the balance of the measurements may be attributed to random fluctuations, unknown variables which may have affected the results, or to a skewed distribution of the measurements.

There was evidence of a significant difference between individual replicate runs in terms of the absolute difference between the recovery measured and 100%, but not for the average recovery of the of the replicates. It is felt that this result was influenced by the replicates from run 29, inlet dynamic spike, in which one set of replicates had recoveries about half as much as the other replicate, indicating that the effect of replication on the difference from 100% recovery is an artifact and may not be important.

TABLE 16. ANALYSIS OF VARIANCE RESULTS USING THE DIFFERENCE BETWEEN 100% AND DYNAMIC SPIKE RECOVERY AS THE DEPENDENT VARIABLE

Source of variation	Sum of squares	DF	Mean of squares	F-ratio	P
Run number	4,146.678	5	829.336	5.086	0.000
Sampling location	1,439.361	1	1,439.361	8.827	0.004
Run number and sampling location interaction	4,257.070	5	851.414	5.221	0.007
Replicate	1,222.266	1	1,222.266	5.221	0.000
Error	16,795.552	103	163.064		
Standard deviation		12.8			
Squared multiple R		0.395			

TABLE 17. NET EFFECTS OF SOURCES OF VARIATION ON THE DIFFERENCE BETWEEN 100% AND DYNAMIC SPIKE RECOVERIES USING ANALYSIS OF VARIANCE MODEL

	Net effect on difference between 100% and recovery	Predicted difference between 100% and recovery
Predicted recovery (no variability)		18.0
Day-to-day variability		
Day 1	-4.20	13.8
Day 2	+6.05	24.0
Day 3	-10.1	7.92
Day 4	-2.05	15.9
Day 5	+8.47	26.5
Day 6	-1.81	16.2
Sampling location		
Inlet	+3.46	21.5
Outlet	-3.46	14.5
Compound		
^{13}-HxCDF	+4.50	22.5
^{13}-OCDF	-1.53	16.5
^{13}-TCDD	-0.78	17.2
^{13}-HxCDD	-3.16	14.8
^{13}-OCDD	-0.96	17.0
Day-sampling location interaction		
Day 1, inlet	-1.86	16.1
Day 1, outlet	+1.86	19.9
Day 2, inlet	+2.99	21.0
Day 2, outlet	-2.99	15.0
Day 3, inlet	-4.33	13.7
Day 3, outlet	+4.33	22.3
Day 4, inlet	-9.55	8.45
Day 4, outlet	+9.55	27.5
Day 5, inlet	+8.52	26.5
Day 5, outlet	-8.52	9.48
Day 6, inlet	-4.24	13.8
Day 6, outlet	+4.24	22.2
Replicate		
Replicate No. 1	+3.91	21.9
Replicate No. 2	-3.91	14.1

SECTION 5

QUALITY ASSURANCE/QUALITY CONTROL

The following QA/QC elements were monitored during this study: surrogate recoveries, blank trains, spiked blanks, initial and routine instrument calibration, and an independently prepared QC check sample.

5.1 SURROGATE RECOVERIES

The results for surrogate recoveries are summarized in Table 18. Because of the large number of determinations obtained during this study, only the average values and the percent relative standard deviations (RSD) for each surrogate from each component of the MM5 sampling train are presented, together with overall average and RSD values.

The overall surrogate recoveries were quantitative, ranging from 67.6% to 146%. A somewhat high bias was found to exist for ^{13}C-1,2,3,7,8-PeCDD; the reasons for this are as yet undetermined. The overall precision of the surrogate recoveries was good, with overall percent RSD values of less than 30%. These results indicate that analysis was successfully conducted.

5.2 BLANK TRAINS

Two blank trains were analyzed. These trains collected ambient air during actual field tests, one each from the inlet and outlet sampling locations. In those cases in which target analytes were detected, less than 0.5 ng was found (Table 19). These results indicate that sampling train contamination problems did not exist during this set of runs.

5.3 SPIKED BLANKS

Performance audit samples independently prepared by the program QAC (Quality Assurance Coordinator) were submitted to laboratory staff for spiking into a blank XAD/filter combination and into reagent grade water. These samples resulted in recoveries of 111% and 98% (Table 20), respectively, indicating adequate proficiency of the laboratory analysts and of the analytical techniques employed.

5.4 QUALITY CONTROL CHECK SAMPLE

Two quality control check samples independently prepared by the QAC or NBS-certified standard reference materials were submitted for analysis by HRGC/HRMS. Analysis of these samples resulted in 99% and 109% recovery (Table 21) of the validated concentration. This is indicative of accurate analytical performance.

TABLE 18. METHOD INTERNAL STANDARD (SURROGATE) RECOVERIES

MM5 train component	^{13}C-TCDF	^{13}C-TCDD	^{13}C-PeCDD	^{13}C-HpCDD
Filter	82.2%[a] (±18%)[b]	73.5% (±17%)	133% (±25%)	65.2% (±20%)
Front half	92.8% (±38%)	85.1% (±39%)	155% (±31%)	75.6% (±28%)
Back half	95.2% (±28%)	86.3% (±29%)	151% (±25%)	67.9% (±25%)
XAD-2	93.5% (±28%)	76.8% (±17%)	144% (±16%)	61.7% (±15%)
Overall	90.9% (±30%)	80.4% (±29%)	146% (±26%)	67.6% (±24%)

[a] Average surrogate recovery for all trains.

[b] Relative standard deviation for all trains.

TABLE 19. MM5 FIELD BLANK TRAINS

Run	Sampling location	Analyte	Amount found (ng) Cyclone/ filter	Probe/ front half	Back half	XAD
29	Outlet	2,3,7,8-TCDF	< 0.005	< 0.004	0.0732	0.0496
		2,3,7,8-TCDD	< 0.007	< 0.004	0.00795	< 0.00346
		1,2,3,7,8-PeCDF	< 0.010	< 0.010	0.0207	0.0252
		1,2,3,7,8-PeCDD	< 0.008	< 0.005	0.0126	< 0.00506
		Total Tetra-CDF	< 0.004	< 0.002	0.287	0.257
		Total Penta-CDF	< 0.004	< 0.008	0.260	0.206
		Total Hexa-CDF	< 0.004	< 0.004	0.187	0.144
		Total Hepta-CDF	< 0.005	< 0.005	0.0434	0.0853
		Total Octa-CDF	< 0.015	< 0.009	0.0585	0.0339
		Total Tetra-CDD	< 0.007	< 0.005	0.0149	0.0372
		Total Penta-CDD	< 0.005	< 0.004	0.0801	< 0.00506
		Total Hexa-CDD	< 0.006	< 0.005	0.0858	0.0673
		Total Hepta-CDD	< 0.007	< 0.008	0.240	0.179
		Total Octa-CDD	0.062	0.047	0.364	0.332
32	Inlet	2,3,7,8-TCDF	< 0.009	< 0.0140	< 0.0322	< 0.00372
		2,3,7,8-TCDD	< 0.014	< 0.0286	< 0.0178	< 0.0126
		1,2,3,7,8-PeCDF	< 0.007	< 0.0292	< 0.0729	< 0.0106
		1,2,3,7,8-PeCDD	< 0.017	< 0.0280	< 0.0282	< 0.0110
		Total Tetra-CDF	< 0.006	< 0.0166	0.183	< 0.00372
		Total Penta-CDF	< 0.007	< 0.0177	0.279	< 0.00597
		Total Hexa-CDF	< 0.012	< 0.0296	0.116	< 0.0104
		Total Hepta-CDF	< 0.021	< 0.0523	0.105	< 0.0128
		Total Octa-CDF	< 0.042	< 0.0833	< 0.0787	< 0.0244
		Total Tetra-CDD	< 0.009	< 0.0319	< 0.0222	< 0.00737
		Total Penta-CDD	< 0.011	< 0.0280	< 0.0360	< 0.00631
		Total Hexa-CDD	< 0.015	< 0.0305	0.0708	< 0.0134
		Total Hepta-CDD	< 0.030	< 0.0593	0.142	< 0.0174
		Total Octa-CDD	< 0.041	< 0.0823	0.319	< 0.0241

TABLE 20. SPIKED BLANK RECOVERIES

Matrix	Analyte	Amount found (pg/μL)	Amount spiked (pg/μL)	Recovery
XAD-2/filter	2,3,7,8-TCDD	75.0	67.8	111%
Water	2,3,7,8-TCDD	66.3	67.8	98%

TABLE 21. QUALITY CONTROL CHECK SAMPLE RECOVERIES

Analyte	Amount found (ng/mL)	Actual concentration (ng/mL)	Recovery
2,3,7,8-TCDD	74.0	67.8	109%
2,3,7,8-TCDD	67.0	67.8	99%

5.5 INSTRUMENT CALIBRATION

An initial four-point calibration curve using standard solutions prepared from pure compounds was analyzed and relative response factors (RRF) calculated. Calibration standards for the initial calibration curve were at nominal concentrations of 5, 10, 100, and 500 ng/mL and included the method and recovery internal standards (at fixed concentrations) together with the static and dynamic spike compounds (at variable concentrations). The relative standard deviation for all compounds from this initial calibration was less than 20%. On every successive day of sample analysis, a 100-ng/mL calibration standard was analyzed before and after all samples were analyzed during that day and the RRFs compared to those from the initial calibration. For most of the daily calibrations, the relative percent difference (RPD) between the standard and the curve did not exceed 20% (Tables 22 to 24).

In addition, a second calibration curve containing native PCDDs and PCDFs was analyzed and accepted using the same criteria as indicated above. This second curve was a three-point curve at nominal concentrations of 5, 10, and 100 ng/mL. Calibration checks were performed sporadically during the project because analysis of native dioxins and furans was not the primary goal of the study. In most cases, the 20% RPD limit for comparison of RRFs between the calibration curve and the daily calibration runs was met (Table 25).

TABLE 22. INITIAL AND CONTINUING CALIBRATION DATA FOR ^{13}C-LABELED PCDD/PCDFs (FIRST CURVE, 3/31/89)

Compound	Initial[a] Avg. RRF	Initial[a] RSD (%)	Continuing (% RPD)[b] 4/3/89 Init.	4/3/89 End	4/4/89 Init.	4/4/89 End	4/5/89 Init.	4/5/89 End	4/6/89 Init.	4/6/89 End	4/7/89 Init.	4/7/89 End	4/10/89 Init.	4/10/89 End	4/11/89 Init.	4/11/89 End	4/19/89 Init.	4/19/89 End	4/20/89 Init.	4/20/89 End	4/21/89 Init.	4/21/89 End	4/24/89 Init.	4/24/89 End
Surrogates																								
^{13}C-2,3,7,8-TCDF	2.459	3.2	7	-10	-1	7	-16	-12	9	16	-7	-9	-3	23	-12	19	-8	-11	-3	37	16	4	-7	6
^{13}C-2,3,7,8-TCDD	2.068	2.3	2	-7	-8	1	10	-15	-1	9	0	-12	6	27	-2	13	-1	-1	-9	33	15	11	8	24
^{13}C-1,2,3,7,8-PeCDD	0.718	4.2	-3	-3	-1	25	-3	9	9	1	-2	-3	11	16	4	16	6	6	-11	11	9	5	4	15
^{13}C-1,2,3,4,6,7,8-HpCDD	0.756	4.2	-14	-7	-11	0	-3	7	-3	-9	5	5	-19	-10	-9	-11	-14	-20	-10	-19	-11	-16	2	-7
Static spike																								
^{13}C-1,2,3,7,8-PeCDF	4.675	9.8	7	5	0	-15	-2	0	-3	3	1	6	-6	4	-39	2	-2	-6	13	17	4	7	9	1
Dynamic spike																								
^{13}C-1,2,3,4,7,8-HxCDF	4.036	9.5	22	9	14	3	1	-6	4	10	-3	-2	23	19	13	21	15	22	7	28	13	23	-5	16
^{13}C-OCDF	1.456	3.7	-2	6	6	3	14	18	9	13	4	6	-2	0	7	-9	-6	-11	-1	2	12	-17	16	-8
^{13}C-1,2,3,4-TCDD	1.708	13	-4	-8	-2	4	-11	-8	5	-9	-9	-5	2	-6	-5	-2	-11	-9	-6	-8	-7	-15	-20	-6
^{13}C-1,2,3,7,8,9-HXCDD	3.224	20	-9	-12	-6	-18	-16	-21	-16	-10	-19	-19	0	-3	-8	-5	-11	-7	-17	-9	-14	-9	-24	-15
^{13}C-OCDD	1.271	6.2	5	6	-8	-10	18	19	19	14	13	11	4	5	11	-9	3	-4	6	13	16	-14	26	3

[a] Indicates initial calibration curve analyzed on 3/31/89.

[b] Indicates daily continuing calibration checks. One calibration check (init.) was analyzed before any samples, and a second check (end) was analyzed after all samples had been analyzed on the indicated date.

TABLE 23. INITIAL AND CONTINUING CALIBRATION DATA FOR ^{13}C-LABELED PCDD/PCDFs (SECOND CURVE, 4/27/89)

Compound	Initial[a] Avg. RRF	Initial[a] RSD (%)	Continuing (% RPD)[b] 4/28/89 Init.	4/28/89 End	5/1/89 Init.	5/1/89 End	5/2/89 Init.	5/2/89 End	5/3/89 Init.	5/3/89 End	5/4/89 Init.	5/4/89 End
Surrogates												
^{13}C-2,3,7,8-TCDF	3.350	11	19	17	-16	8	-17	-4	-23	NA	-20	34
^{13}C-2,3,7,8-TCDD	2.878	9.8	15	29	-16	11	-26	0	-21	NA	-18	25
^{13}C-1,2,3,7,8-PeCDD	1.028	6.3	19	25	-10	14	-15	-1	-9	NA	-6	3
^{13}C-1,2,3,4,6,7,8-HpCDD	0.520	7.1	9	13	7	17	-2	6	10	NA	-1	-10
Static spike												
^{13}C-1,2,3,7,8-PeCDF	4.669	8.7	-1	2	1	1	3	4	-4	NA	-3	8
Dynamic spike												
^{13}C-1,2,3,4,7,8-HxCDF	7.283	8.8	1	-9	-11	-6	-8	-8	-12	NA	-2	8
^{13}C-OCDF	1.418	12	16	11	-7	4	6	6	6	NA	5	-8
^{13}C-1,2,3,4-TCDD	1.792	11	-8	-12	-8	-18	1	-9	-10	NA	-6	-15
^{13}C-1,2,3,7,8,9-HxCDD	4.150	14	-14	-20	-16	-15	-9	-16	-7	NA	6	-3
^{13}C-OCDD	1.111	16	18	16	22	7	14	7	9	NA	12	-5

[a] Indicates initial calibration curve analyzed on 4/27/89.
[b] Indicates daily continuing calibration checks. One calibration check (init.) was analyzed before any samples, and a second check (end) was analyzed after all samples had been analyzed on the indicated date.
NA = Not analyzed.

TABLE 24. INITIAL AND CONTINUING CALIBRATION DATA FOR ^{13}C-LABELED PCDD/PCDFs (THIRD CURVE, 5/8/89)

Compound	Initial[a] Avg. RRF	Initial[a] RSD (%)	Continuing (% RPD)[b] 5/9/89 Init.	5/9/89 End	5/17/89 Init.	5/17/89 End	5/18/89 Init.	5/18/89 End	5/19/89 Init.	5/19/89 End
Surrogates										
^{13}C-2,3,7,8-TCDF	3.222	4.7	34	17	13	33	6	1	20	-2
^{13}C-2,3,7,8-TCDD	2.728	6.9	24	-7	7	21	5	1	12	-9
^{13}C-1,2,3,7,8-PeCDD	0.837	7.5	10	18	11	10	1	3	8	-8
^{13}C-1,2,3,4,6,7,8-HpCDD	0.633	1.6	5	-2	-15	-8	-6	1	-6	2
Static spike										
^{13}C-1,2,3,7,8-PeCDF	4.821	13	-3	-10	-6	5	-7	-1	3	9
Dynamic spike										
^{13}C-1,2,3,4,7,8-HxCDF	5.08	1.1	-4	6	7	8	-3	-5	2	-3
^{13}C-OCDF	1.558	5.6	9	3	-7	-10	-5	-5	-16	-8
^{13}C-1,2,3,4-TCDD	1.616	7.2	-10	-2	-3	-24	-10	0	2	6
^{13}C-1,2,3,7,8,9-HxCDD	3.241	9.2	-7	-5	6	2	-4	-6	9	-11
^{13}C-OCDD	1.262	7.5	16	8	7	8	13	10	2	7

[a] Indicates initial calibration curve analyzed on 5/8/89.
[b] Indicates daily continuing calibration checks. One calibration check (init.) was analyzed before any samples, and a second check (end) was analyzed after all samples had been analyzed on the indicated date.

TABLE 25. INITIAL AND CONTINUING CALIBRATION DATA FOR NATIVE PCDD/PCDFs

Compound	Initial[a] Avg. RRF	Initial[a] RSD (%)	Continuing (% RPD)[b] 4/12/89 init.	4/21/89 init.	5/2/89 init.	5/8/89 init.	5/17/89 init.	5/19/89 init.
Individual congeners								
2,3,7,8-TCDF	2.493	3.8	-6	-16	-14	-11	-4	-8
2,3,7,8-TCDD	2.07	4.2	18	-2	7	0	13	11
1,2,3,7,8-PeCDF	3.56	3.2	-5	12	-1	9	18	68
1,2,3,7,8-PeCDD	3.089	1.7	-1	-1	2	-2	4	54
Congener groups								
Total Tetra-CDF	2.493	3.8	-6	-16	-14	-11	-4	-8
Total Penta-CDF	4.902	9.7	-7	4	-28	-21	-14	22
Total Hexa-CDF	5.84	2.8	-5	-17	48	36	27	-42
Total Hepta-CDF	4.322	0.54	-3	-10	28	14	6	-46
Total Octa-CDF	1.964	7.2	-2	-9	8	-3	-5	-50
Total Tetra-CDD	2.07	4.2	18	-2	7	0	13	11
Total Penta-CDD	3.089	1.7	-1	-1	2	-2	4	54
Total Hexa-CDD	4.541	3.3	-1	-14	31	18	24	-42
Total Hepta-CDD	2.552	1.3	-4	-13	7	5	-1	-51
Total Octa-CDD	1.987	6.4	0	-11	-9	-20	-5	-49

[a] Indicates initial calibration curve analyzed on 4/6/89.

[b] Indicates daily continuing calibration checks. One calibration check (init.) was analyzed before any samples, and a second check (end) was analyzed after all samples had been analyzed on the indicated date.